

Evaluation of Lime and Persulfate Treatment for Mixed Contaminant Soil from Plum Brook Ordnance Works (Sandusky, OH)

Victor F. Medina, Scott A. Waisner, Agnes B. Morrow, Catherine C. Nestler, and Michael Jones

September 2007



Evaluation of Lime and Persulfate Treatment for Mixed Contaminant Soil from Plum Brook Ordnance Works (Sandusky, OH)

Victor F. Medina, Scott A. Waisner, and Agnes B. Morrow

Environmental Laboratory U.S. Army Engineer Research and Development Center 3909 Halls Ferry Road Vicksburg, MS 39180-6199

Catherine C. Nestler

Applied Research Associates, Inc., Southern Division 119 Monument Place Vicksburg, MS 39180

Michael Jones

Alcorn State University
Alcorn State, MS 39096-7500

Final report

Approved for public release; distribution is unlimited.

Abstract: The former Plum Brook Ordnance Works in Sandusky, OH, manufactured explosives from 1941 to 1945. The Reservoir No. 2 Burning Ground has soil contaminated with explosives, 2,4,6-trinitrotoluene (TNT) and 2,4-/2,6-dinitrotoluene (DNT), a polychlorinated biphenyl (PCB), Araclor 1260, polycyclic aromatic hydrocarbons (PAHs), particularly benzo(a)pyrene, and lead. The U.S. Army Engineer Research and Development Center (ERDC) Environmental Laboratory (EL) investigated a series of chemical based treatments to address this complex matrix. Lime treatment was tested to treat the explosives. Advanced oxidation (persulfate treatment and Fenton's reagent) was studied for treatment of PCBs and PAHs. Phosphate treatment was investigated for stabilizing lead. Lime treatment degraded 98 percent of TNT, 75 percent of DNT, and 80 percent of PCBs. There was minimal removal of PAHs (41 percent). Similar removal levels were found for persulfate treatment and lime followed by persulfate. Lower destruction rates of explosives were obtained by a single Fenton's reagent treatment, probably due to rapidity of the reaction. Loss percentages were roughly the same for highly contaminated soils (burn layer) and less contaminated soil (west surface soil). Treatments of the most contaminated soil (burn layer soils) did not meet Preliminary Remediation Goals for explosives or PCBs. Phosphate treatment was effective at stabilizing the lead in the soil, reducing lead toxicity characteristic leaching procedure concentrations below 5 mg/L.

DISCLAIMER: The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

DESTROY THIS REPORT WHEN NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

Contents

Fig	Figures and Tablesv				
Pr	Prefacevii				
Ac	cronymsviii				
Un	nit Conversion Factors	x			
1	Introduction	1			
	Site background				
	Contaminant characterization	3			
	Explosives	4			
	Polychlorinated biphenyls (PCBs)	5			
	Polycyclic aromatic hydrocarbons (PAHs)	6			
	Metals (lead)	8			
	Remediation technologies	10			
	Alkaline hydrolysis	10			
	Persulfate oxidation	15			
	Fenton's reagent	18			
	Stabilization of lead with phosphate	21			
2	Experimental Design	22			
	Objectives	22			
	Design	22			
3	Materials and Methods	24			
	Soil preparation	24			
	Analysis methods	25			
	Explosives	25			
	PCBs	26			
	PAHs	26			
	Metals (lead)	27			
	Statistical analysis	27			
	Lime dosing experiments	27			
	Slurry experiments	28			
	Reactor assembly	28			
	Alkaline hydrolysis	29			
	Lime/persulfate oxidation	29			
	Modified-Fenton oxidation	30			
	Cobble treatment				
	Phosphate stabilization	30			

iv

4	Results	31			
	Initial contaminant concentrations	31			
	Alkaline hydrolysis	32			
	Lime dosing experiment	32			
	Lime slurry experiment	32			
	Persulfate oxidation	35			
	Lime/persulfate oxidation	36			
	Discussion	36			
	Comparison of treatment variation on contaminant removal	40			
	Modified-Fenton oxidation	42			
	Cobble treatment	44			
	Phosphate stabilization	44			
5	Discussion	46			
	Comparison of alkaline hydrolysis and persulfate oxidation	46			
	Alkaline hydrolysis of PCBs				
	Potential of Fenton oxidation	49			
	Lead co-contamination	49			
	Field application	50			
6	Conclusions	52			
References					
Аp	pendix A: Draft Engineering Evaluation/Cost Analysis Report for Reservoir No. 2				
•	Burning Ground, PBOW	62			
Re	eport Documentation Page				

Figures and Tables

Figures

Figure 1. Location of the former Plum Brook Ordnance Works (used with permission of Jacobs Engineering Group).	2
Figure 2. Location of the Reservoir No. 2 Burning Ground within Plum Brook Ordnance Works (used with permission of Jacobs Engineering Group)	3
Figure 3. Structures of relevant explosive contaminants of concern	
Figure 4. Generalized chemical structure of polychlorinated biphenyl (PCB) compounds	6
Figure 5. Structure of benzo(a)pyrene, a 5-ring polycyclic aromatic hydrocarbon (PAH), adapted from Pitot and Dragan (1996).	7
Figure 6. Solubility of common lead compounds by pH with both the TCLP and the UTS for lead indicated	9
Figure 7. Alkaline hydrolysis of TNT. Top – excess base, bottom – excess TNT (modified from Saupe et al. 1998; NRC 1999; Felt et al. 2001a; Davis et al. 2007 in press)	11
Figure 8. Reaction of PCB with nucleophile (top) and an alkoxide (bottom), after Hutzinger et al. (1974).	13
Figure 9. Alkaline hydrolysis of PCB with a co-solvent (after Brunelle et al. 1985)	13
Figure 10. Production of sulfate free radicals from persulfate and catalyzed by ferrous iron.	16
Figure 11. Fenton's reaction.	18
Figure 12. Fenton's reaction with organic compounds (from Neyens and Baeyens 2003)	19
Figure 13. Proposed treatment train for contaminated soil from Plum Brook Ordnance Works.	23
Figure 14. Steps in soil processing	25
Figure 15. Comparison of cobble material and ground soil	26
Figure 16. Soil slurry reactor.	29
Figure 17. Results of the lime dosing experiment.	32
Figure 18. Results of the hydrated lime slurry treatment of Burn Layer Soil 1	34
Figure 19. Results of the hydrated lime slurry treatment of West Surface Soil 2	34
Figure 20. Results of persulfate slurry treatment of Burn Layer Soil 1 at 40 °C	37
Figure 21. Results of persulfate slurry treatment of West Surface Soil 2 at 40 °C.	37
Figure 22. Removal of organic compounds from Burn Layer Soil 1 through a combination of alkaline hydrolysis and persulfate oxidation at 25 °C.	38
Figure 23. Removal of organic compounds from Burn Layer Soil 1 through a combination of alkaline hydrolysis and persulfate oxidation at 40 °C.	39
Figure 24. Final concentration of TNT in Burn Layer Soil 1 after each treatment.	41
Figure 25. Final concentration of DNT in Burn Layer Soil 1 after each treatment	41
Figure 26. Final concentration of PCB-Aroclor 1260 in Burn Layer Soil 1 after each treatment	42

Figure 27. Temperature profile of Fenton reaction during treatment of PBOW soil	43
Figure 28. Comparison of explosives concentrations from solid and ground cobbles by water and solvent extraction	44
Figure 29. TCLP for lead following phosphate stabilization of lime-treated soil	45
Figure 30. Schematic of conceptual field application.	51
Tables	
Table 1. Preliminary remediation goals established by USEPA Region 9	4
Table 2. Selected physical and chemical characteristics of TNT and the DNT1	5
Table 3. Relevant physical and chemical data on the PCB Aroclor 1260 (ATSDR 2000)	6
Table 4. Selected physical and chemical properties of benzo(a)pyrene (ATSDR 2001)	8
Table 5. Solubility of selected lead minerals.	10
Table 6. Initial concentration of organic compounds in untreated soil and the relative standard deviation (%) based on units of mg/kg	31
Table 7. Initial concentration of lead in untreated soil expressed as both total and leachable lead and the relative standard deviation (%) based on five replicates	31
Table 8. Removal of organic compounds by alkaline hydrolysis	35
Table 9. Removal of organic compounds by thermally activated persulfate (40 °C)	38
Table 10. Concentration of explosives found in solution during the combined alkaline hydrolysis/persulfate oxidation of burn layer soil.	40
Table 11. Effect of experimental conditions on lime hydrolysis/persulfate oxidation of burn layer soil	40
Table 12. Results of Fenton oxidation of PBOW burn layer soil	43

ERDC/EL TR-07-19 vii

Preface

This report stems from experimental work conducted under a cooperative research and development agreement (CRADA) with Jacobs Engineering Group, Inc. (JEG). JEG's client was the Huntington District of the Army Corps of Engineers. The JEG personnel assigned to the Plum Brook project were Doug Hodge, Al Hardesty, and Bratati Lynn. The authors wish to thank Hodge, Hardesty, and Lynn for providing background data and soil samples, and Allyson Harrison for PAH analysis. Thanks are also expressed to Lannae Long (CELRN-EC-R) and Chuck Coyle (Omaha CX) for bringing to our attention the USEPA documents concerning alkaline hydrolysis of PCBs.

This research effort was directed by Dr. Victor F. Medina under the oversight of the Remediation/Management of Distributed Source of Ordnance Related Compounds (ORC) on Ranges work unit managed by Dr. Jeffrey Davis.

This report was prepared by Dr. Medina and Scott A. Waisner, Environmental Engineering Branch, Environmental Processes and Engineering Division (EPED), Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC); Agnes B. Morrow, Environmental Chemistry Branch, EL; and Catherine C. Nestler, Applied Research Associates, Inc. Deborah Felt and W. Andy Martin, Environmental Engineering Branch, provided in-house review. Technical assistance was provided by Michael Jones of Alcorn University.

This study was conducted under the direct supervision of Dr. Patrick Deliman, Chief, Environmental Engineering Branch, and under the general supervision of Dr. Richard E. Price, Chief, EPED, and Dr. Elizabeth C. Fleming, Director, EL.

COL Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

ERDC/EL TR-07-19 viii

Acronyms

ADNT aminodinitrotoluene

AOP advanced oxidation process

BAP benzo(a)pyrene

2BG Reservoir No. 2 Burning Ground

BGS below ground surface

COC contaminant of concern

CY cubic yards

DNT 2,4- or 2,6-dinitrotoluene

EL Environmental Laboratory

ERDC U.S. Army Engineer Research and Development Center

ISCO in situ contaminant oxidation

JEG Jacobs Engineering Group, Inc.

mg/kg milligrams per kilogram (ppm)

mg/L milligrams per liter (ppm)

NASA National Aeronautics and Space Administration

ORC ordnance related compound

PAH polycyclic aromatic hydrocarbon

PBOW Plum Brook Ordnance Works

PCB polychlorinated biphenyl

PCDD polychlorinated dibenzodioxin

PCDF polychlorinated dibenzofuran

PRG Preliminary Remediation Goal

RDX hexahydro-1,3,5-trinitro-1,3,5-triazine

TCLP toxicity characteristic leaching procedure

TNT 2,4,6-trinitrotoluene

μg/g micrograms per gram

μg/kg micrograms per kilogram (ppb)

 $\mu g/L$ micrograms per liter (ppb)

USACE U.S. Army Corps of Engineers

USEPA U.S. Environmental Protection Agency

UTS universal treatment standard

Unit Conversion Factors

Multiply	Ву	To Obtain
acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(°F-32)/1.8	degrees Celsius
feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
hectares	1.0 E+04	square meters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
pounds (mass) per square foot	4.882428	kilograms per square meter
pounds (mass) per square yard	0.542492	kilograms per square meter
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters
tons (long) per cubic yard	1,328.939	kilograms per cubic meter
tons (2,000 pounds, mass)	907.1847	kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
yards	0.9144	meters

1 Introduction

Site background

The former Plum Brook Ordnance Works (PBOW) is located south of Sandusky, OH (Figure 1). From 1941 to 1945, PBOW functioned as a manufacturing plant for 2,4,6-trinitrotoluene (TNT), 2,4- and 2,6 dinitrotoluene (2,4/2,6-DNT), and pentolite. The activities at the works have left contaminated surface soils and groundwater. The National Aeronautics and Space Administration (NASA) acquired PBOW in 1963 and operates the site as the Plum Brook Station (PBS) of the John Glenn Research Center, Lewis Field, Cleveland, OH. NASA utilizes about 6,400 acres for conducting space research.

The area of concern for this study was a disposal and burn area for production process wastes called the Reservoir No. 2 Burning Ground (2BG), with an area of about 25,000 ft2. The 2BG site is located in the northwestern portion of PBOW (Figure 2). It is not known when the site was first used for burning; however, a 1950 aerial photo clearly shows the site to be in existence and photographs dated as late as 1962 show ongoing operations. Burning activities ceased in 1962. Limited restoration of the site was performed in 1963 when the area was cleared of debris and the ground restored to proper grade. The 2BG site was used temporarily as a baseball field by NASA and is currently a grass-covered open field with young hardwood trees and surrounding brush. There is a drainage ditch at the northern edge of the field. 2BG is surrounded on all sides by NASAcontrolled property, which is fenced and maintained by security on a 24-hr basis. The area surrounding the site is wooded and is not being utilized by NASA. The U.S. Department of Agriculture uses a few adjacent clearings north and west of the site on a periodic basis as wildlife research plots. There are no facilities being operated by NASA within 2,000 ft of 2BG. The intent is to sell the site and make it available to the public for unrestricted use.

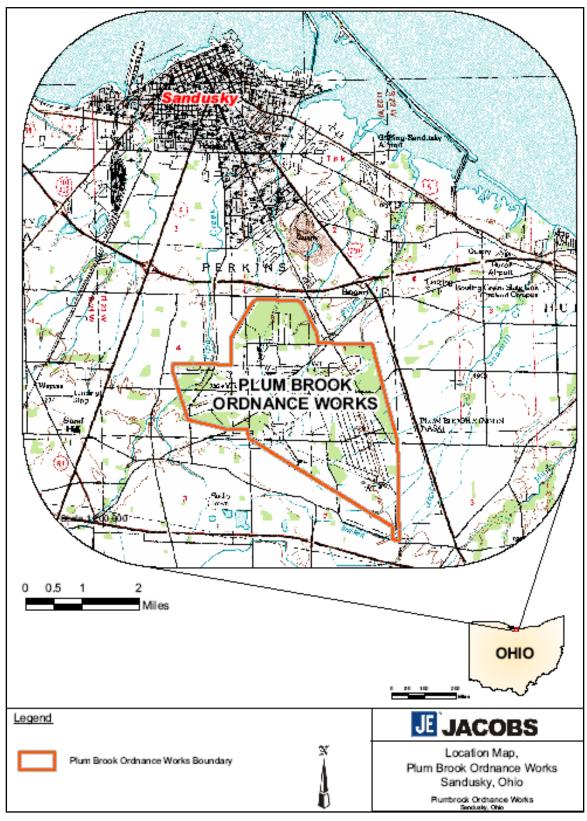


Figure 1. Location of the former Plum Brook Ordnance Works (used with permission of Jacobs Engineering Group).

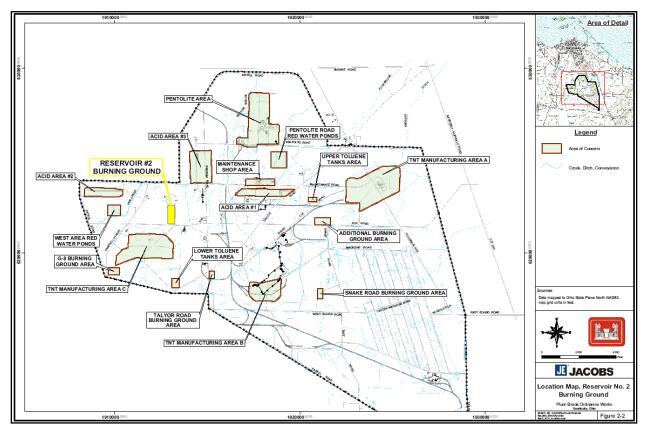


Figure 2. Location of the Reservoir No. 2 Burning Ground within Plum Brook Ordnance Works (used with permission of Jacobs Engineering Group).

Contaminant characterization

Preliminary sampling during initial site characterization (JEG 2006; Appendix A, this report) consisted of four samples of the surface soil of the burn area, 10 samples from the burn soil layer, and 11 samples from the subsurface soil of the burn area. An additional 22 surface soil samples were taken outside the burn area, and 18 samples were taken from the subsurface soil outside the burn layer.

Soil contamination at 2BG is concentrated within the footprint of the former burn area. The burn layer is approximately 1 ft below ground surface (BGS) and averages 1 ft in thickness. Contamination within the burn area is confined primarily to the burn layer material and, to a lesser extent, in the surface soil above the burn layer. Contamination is also present in surface soil west of the burn area. The amount of hazardous soil from within the footprint of the burn area and from selected surface hotspots west of the burn area is estimated to be 1,816 cubic yards (CY).

Several contaminants exceeded the United States Environmental Protection Agency (USEPA) Region 9 Residential Preliminary Remediation Goals (PRGs). These PRGs are not binding regulatory limits, but are increasingly being used as de facto treatment limits in the absence of actual risk assessment data. The residential and industrial PRGs for explosives, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and lead are listed in Table 1 along with the results of the 2BG contaminant characterization. The source document for these PRGs is available from the USEPA (2004) online at:

http://www.epa.gov/region09/waste/sfund/prg/files/04prgtable.pdf.

Contaminant	Residential PRG (mg/kg)	Industrial PRG (mg/kg)	2BG Average Concentration (mg/kg)
TNT	16	57	35,400
2,4-DNT	120	1,200	9,700
2,6-DNT	61	620	1,400
PCB (Aroclor 1260)	0.22	0.74	44.4
PAH (BaP)	0.062	0.21	0.085
Lead	400	800	551 to 11,930

Table 1. Preliminary remediation goals established by USEPA Region 9.

Explosives

Preliminary site contaminant analysis conducted by the Jacobs Engineering Group (JEG 2006) found concentrations of 2,4-DNT and TNT in the burn layer material ranging from less than 1 percent to 4.5 percent by mass. Explosives concentrations were considerably lower in the surface soil above the burn layer. A few isolated areas of contamination were also present in the surface soil west of the burn area. The structures of the explosive contaminants of concern and two of the degradation products are shown in Figure 3. Relevant physical and chemical data are provided in Table 2.

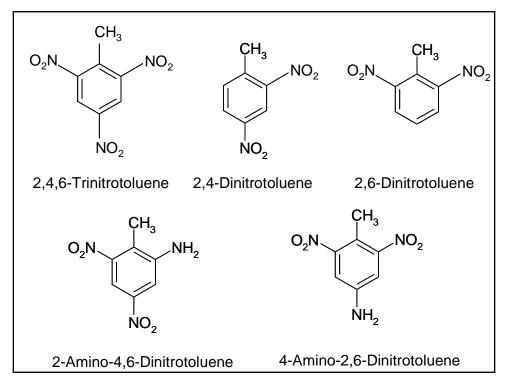


Figure 3. Structures of relevant explosive contaminants of concern.

Table 2. Selected physical and chemical characteristics of TNT and the DNT1.

Parameter	TNT	2,4-DNT	2,6-DNT
Empirical formula	C7H5N3O6	C7H6N2O4	C7H6N2O4
Molecular weight (g/mol)	227.13	182.14	182.14
Aqueous solubility 25 °C (mg/L)	100.5	280	208
Adsorption coefficient (Kd) to Sharkey clay surface soil (L/kg)	10.0	12.5	5.96
¹ Extracted from: McGrath 1995; Brannon and Pennington 2002.			

TNT is considered to be both mutagenic and a Class C carcinogen (Agency for Toxic Substances and Disease Registry (ATSDR) 1995) and the USEPA list TNT as a priority pollutant (USEPA-IRIS 1997). Major et al. (2002) reviewed the environmental effects of TNT and concluded that plants accumulate TNT, but TNT is not biomagnified.

Polychlorinated biphenyls (PCBs)

A generalized PCB structure is shown in Figure 4. The primary PCB found on site is Aroclor 1260. Site contaminant analysis found concentrations of PCBs are greatest in the surface soil above the burn layer and in the surface soil outside of the burn area. All the soil samples analyzed

exceeded the residential PRG. Physical and chemical data for Aroclor 1260 are provided in Table 3.

An important physical property of PCBs is their inertness; PCBs resist both acid and alkaline degradation, and are thermally stable (Hutzinger et al. 1974). The PCBs are relatively insoluble in water and this solubility decreases with increasing chlorination. PCBs have a high potential for bioaccumulation, but they do not appear to be toxic to plants. Positive carcinogenicity studies in rats have resulted in classification of PCBs in general as B2, probable human carcinogens (ATSDR 2000). A significant health impact also derives from the by-products of the combustion of PCBs. These by-products include hydrogen chloride and the highly toxic polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Four samples of site soil contaminated with PCB-Aroclor 1260, analyzed for combustion by-products, resulted in total PCDF concentrations that ranged from 0.8 to 5.6 $\mu g/g$.

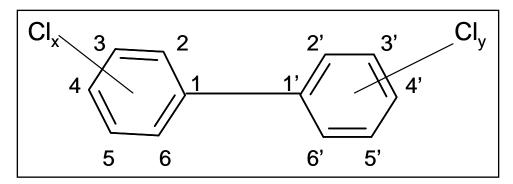


Figure 4. Generalized chemical structure of polychlorinated biphenyl (PCB) compounds.

Molecular weight	358	Partition coefficient: log Kow	6.8
Color	Light yellow	Vapor pressure, mm Hg at 25 °C	4.05 x 10 ⁻⁵
Physical state	Sticky resin	Solubility in water (mg/L)	0.08 at 24 °C
Boiling point (°C)	385-420	Solubility in organic solvent	Very soluble
Density at 25 °C (g/cm ³)	1.62	Chlorine content	60% by weight

Table 3. Relevant physical and chemical data on the PCB Aroclor 1260 (ATSDR 2000).

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs), in general, are large, multi-ring compounds characteristically nonpolar, neutral, and hydrophobic. They are composed of two or more benzene rings fused in a linear, stepped or cluster arrangement (Figure 5). Volatilization can remove the lighter-

molecular-weight homologues (2-rings). The higher-molecular-weight compounds are increasingly resistant to chemical and biological degradation (4- and 5-rings). Another chemical property, pertinent to remediation, is that PAHs bind tightly to the humic fraction of soil (Alexander and Alexander 2000; Bogan and Sullivan 2003). This binding strength increases with exposure time making aged soils more difficult to remediate. The persistence of PAHs in the environment, coupled with their hydrophobicity, gives them a high potential for bioaccumulation. As a class of compounds, PAHs are listed as carcinogens, mutagens, and immunosuppressants with the toxicity dependent on the chemical structure (ATSDR 2001).

Concentrations of the PAH compound benzo(a)pyrene (BaP) at the Plum Brook site exceeded the residential PRG in the burn pit area and the industrial PRG in the area west of the burn pit. BaP is one of the most researched and one of the more toxic human carcinogens. It is used as the baseline reference for the Toxic Equivalency Factors of PAHs (Nisbet and LaGoy 1992). Relevant physical and chemical data on BaP are provided in Table 4.

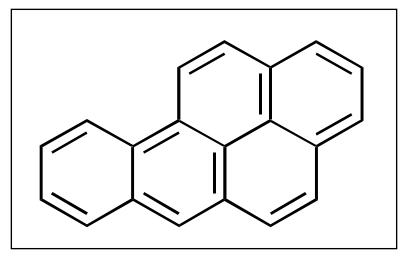


Figure 5. Structure of benzo(a)pyrene, a 5-ring polycyclic aromatic hydrocarbon (PAH), adapted from Pitot and Dragan (1996).

Physical	Yellow green powder
	Boiling point: 495 °C
	Melting point: 177 °C
Chemical	Solubility in water: <0.1 mg/L
	Percentage volatiles by volume: low
Reactivity	Stable
	Avoid strong oxidizing agents
	Hazardous decomposition products: CO, CO ₂ on combustion
Toxicity Suspected human carcinogen; known laboratory animal carcinog	

Table 4. Selected physical and chemical properties of benzo(a)pyrene (ATSDR 2001).

Metals (lead)

Concentrations of lead at Plum Brook 2BG are greatest within the burn layer material. The total lead concentration in the burn layer ranged from 1,100 to 3,300 mg/kg, which exceeds the residential PRG of 400 mg/kg. Elevated concentrations of lead are also present in the surface soil above the burn layer and in a few isolated areas in the surface soil west of the burn area (211 to 333 mg/kg). Even at very low levels, lead has been linked to subtle developmental delays and reduced mental function in children (USEPA 2001; ATSDR 2005). The threshold toxicity characterization concentration for lead in contaminated soils established by the Toxicity Characteristic Leaching Procedure (TCLP) is 5.0 mg/L and the universal treatment standard (UTS) for lead is 0.75 mg/L (ITRC 2003).

Lead is an amphoteric metal that exhibits its greatest solubility in strongly acidic (pH < 4) and alkaline (pH > 11) solutions. Under acidic conditions, elemental lead will dissolve, releasing a hydrated cation, Pb²⁺. Under alkaline conditions, elemental lead will dissolve, under most circumstances, to form a lead hydroxide complex. Lead that exists in the dissolved state can be sorbed to negatively-charged clay particle surfaces. Thus, the erosion and surface water transport of contaminated clays can be a major source of lead mobility in the environment, and environmental transport can be either attenuated or increased depending upon the mobility of the clay particles.

The speciation of metals in a soil is a major factor affecting concentration of the metals in the pore water. Metal speciation in the soil is influenced by hydrogen-ion concentration (pH) and redox potential (Eh) within the soil. Figure 6 illustrates the pH dependence and amphoteric nature of common

lead salt compounds. For example, the orthophosphate ion forms sparingly soluble solids with several metals, including lead (Yang et al. 2001; Hettiarachichi et al. 2002; Tardy et al. 2003). Effective remediation may not require complete conversion of soil lead to insoluble ore-like forms, but rather only transformation of the most chemically and/or biologically reactive or labile forms for lead (Laperche et al. 1996).

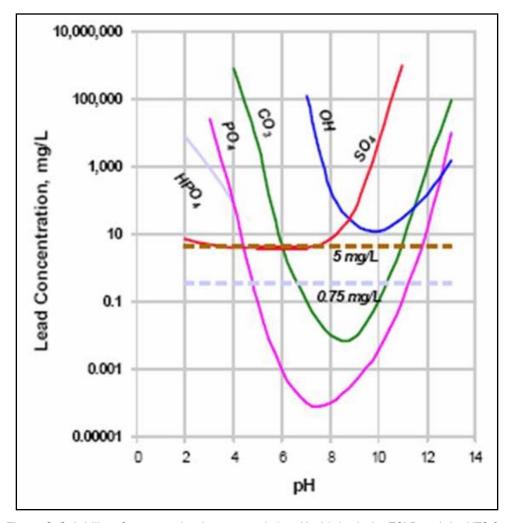


Figure 6. Solubility of common lead compounds by pH with both the TCLP and the UTS for lead indicated.

Table 5 lists the formulas and the logarithm of the solubility products of several commonly found lead salts and minerals. Most common salts of lead are relatively insoluble or only slightly soluble, with the notable exceptions of lead nitrate and lead acetate. Lead phosphate minerals are some of the most insoluble solids known to form under typical geochemical conditions.

Mineral **Formula** Log K_{sp}¹ Lead acetate $Pb(C_2H_3O_2)$ 1.0 8.0 Lead nitrate Pb(NO₃) PbCl₂ -4.8 Lead chloride PbO -14.9 Litharge (lead oxide) PbSO₄ -7.7 Anglesite (lead sulfate) PbCO₃ -12.8 Cerussite (lead carbonate) Pb(PO₄)₂ -43.5 Lead orthophosphate Pyromorphite Pb₅(PO₄)₃Cl -84.4 Pb5(PO4)3OH -76.8 Hydroxypyromorphite Pb5(PO4)3F -71.6 Fluoropyromorphite Bromopyromorphite Pb₅(PO₄)₃Br -78.1 Corkite PbFe₃(PO₄)(SO₄)(OH)₆ -112.6 Hindsalite PbAl₃(PO₄)(SO₄)(OH)₆ -99.1 -99.3 Plumbogummite PbAI₃(PO₄)₂(OH)₅·H₂O ¹ From Traina and Laperche 1999.

Table 5. Solubility of selected lead minerals.

Remediation technologies

As part of the 2BG treatability study, technologies were screened to identify those that could meet the remedial objectives. Based on this screening, several promising technologies were evaluated. The treatability study involved the collection of bulk samples from the 2BG site, pretreatment chemical analysis, batch reactor studies, and post-treatment chemical analysis to gauge the treatment effectiveness. The batch reactor studies evaluated the following treatments:

- lime slurry (alkaline hydrolysis) targeting explosives
- persulfate slurry (advanced oxidation) targeting PCBs and PAHs
- Fenton's reagent (advanced oxidation) targeting all organic contaminants
- phosphate –Enviroblend® (stabilization/immobilization) targeting lead

Alkaline hydrolysis

Explosives

The alkaline hydrolysis of nitroaromatic compounds (Figure 7) is a heterolytic substitution resulting from nucleophilic attack by an alkaline

anion. Homolytic substitutions involve the reaction of uncharged free radicals and probably occur simultaneously with the heterolytic substitution (NRC 1999). TNT has a strong electron-withdrawing nature due to the presence of the multiple nitro groups, which allows it to react with many soil components. The symmetrical placement of the nitro groups hinders chemical attack on the ring but, at the same time, these nitro groups are susceptible to reductive transformation (Emmrich 1999, 2001; Karasch et al. 2002; Thorne et al. 2004). Although the base hydrolysis of TNT is probably a complex series of reactions, reaction pathways can be inferred from the identification of intermediates (Figure 7). The pathways and products differ depending on whether the base or the TNT is in excess.

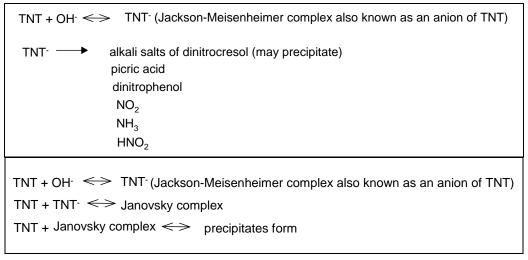


Figure 7. Alkaline hydrolysis of TNT. Top – excess base, bottom – excess TNT (modified from Saupe et al. 1998; NRC 1999; Felt et al. 2001a; Davis et al. 2007 in press).

Janovsky (1891) first established the transformation of TNT in basic solutions. The need for a simple and economical treatment technology for application to ranges and explosives/energetics production facilities was the impetus for more recent studies in alkaline destruction of explosives and energetics. Saupe et al. (1998) used harsh reaction conditions, including elevated temperature and pressure to achieve complete degradation of the TNT. The addition of hydrated lime (Ca(OH)₂) is an inexpensive means to achieve the alkaline conditions required for the reaction without the harsh reaction conditions (Davis et al. 2006). Arienzo (1999) reported complete removal of TNT from soil in 10 min with the application of 1 percent by weight of Ca(OH)₂. Emmrich (1999, 2001) also treated TNT and RDX in solution and soils with calcium hydroxide at

20 °C with nitrite and nitrate formation appearing as end products. Felt et al. (2001a, 2001b, 2002) and Hansen et al. (2001) studied the alkaline hydrolysis of explosives in solution as a first step in establishing the feasibility of chemical remediation of soils at firing ranges and former munitions plants. At pH 10, an initial TNT concentration of 25 ppm was reduced in half after 24 hr. Nearly instantaneous transformation of TNT was achieved when pH levels greater than 11 were used. The reaction products are environmentally benign compounds that include nitrite, nitrate, and organic acids, such as formate (Hansen et al. 2003). Current research focuses on the reaction in soil at ambient temperature/pressure under field conditions (Thorne et al. 2004; Larson et al. 2007; Johnson et al. 2006, in press). Because the alkaline hydrolysis reaction occurs in the aqueous phase, the topically placed amendment must first dissolve into the soil pore water before the reaction can take place. Once dissolved, OH- ions can then interact with the energetic compound.

Emmrich (2001) and Davis et al. (2006) examined alkaline hydrolysis of co-contaminants and degradation products of TNT, the DNTs, and ADNTs. These authors reported that while both sets of compounds are more resistant than TNT to the nucleophilic substitution reaction of alkaline hydrolysis, the ADNTs are more reactive than the DNTs. These compounds can be treated by alkaline hydrolysis under field conditions if the treatment pH is increased or, under ex situ conditions, by increasing the treatment temperature.

Polychlorinated biphenyls (PCBs)

The treatment of PCBs by alkaline hydrolysis is a controversial topic. While there are many articles that describe reactions and successful PCB degradation, other articles suggest that transformation is limited and removals are due to volatilization of the PCB. Hutzinger et al. (1974) outlined the reaction of PCBs with alkoxides, a nucleophilic displacement of the chlorine atoms (Figure 8). Due to their general chemical inertness, many of the PCB reactions require the addition of substantial thermal energy. Manchak (1978) and Thyagarajan (1983) entered patent applications on cleaning transformer oils that involved the destruction of PCBs by alkaline hydrolysis at ambient temperatures. Thyagarajan (1983) treated PCB liquids with either potassium or sodium hydroxide (KOH or NaOH) and then filtered the solution through diatomaceous earth or activated alumina. The PCB reacts with the hydroxyl ion to form a hydroxylated biphenyl that is absorbed during the filtering process.

Figure 8. Reaction of PCB with nucleophile (top) and an alkoxide (bottom), after Hutzinger et al. (1974).

Brunelle and Singleton (1985) and Brunelle et al. (1985) reported on alkaline hydrolysis of PCBs in soil that also employed a co-solvent, polyethylene glycol (PEG). This reaction used a 3:1 (w/w) concentration of KOH/PEG (Figure 9). An initial nucleophilic aromatic substitution reaction resulted in the methoxylation of the PCB at two of the chlorine sites. The methoxylated PCB continued to react with the excess KOH, resulting in ring cleavage and the production of a polyglycol. The reaction proceeded slowly unless heat was added. It also required that the soil or sediment be dried before treatment. The authors compared PCB congeners with different chlorination concentrations and reported that the treatment works best on compounds with higher chlorine levels, i.e., the treatment worked better with Aroclor 1260 than with Aroclor 1254. They did not report any toxicity testing of the final product and glycol phenols have the potential, due to their high water solubility, for migration into groundwater.

Figure 9. Alkaline hydrolysis of PCB with a co-solvent (after Brunelle et al. 1985).

Payne et al. (1991) reported the complete dehalogenation of PCBs in soil at ambient temperature. They used quicklime that they "hydrophobized" by treatment with fatty acid, creating a granular substrate easily mixed into the soil/sediment/sludge. The fatty acid absorbed and immobilized the PCB and then delayed and slowed the exothermic hydration reaction that produced the calcium hydroxide. The calcium hydroxide, which is in close proximity to the PCB molecule, initiated the dehalogenation reactions. Laboratory experiments on contaminated soils at ambient temperatures indicated a reaction time of several months, depending on the PCB concentration. Increasing the temperature of the reaction increased the destruction rate, reducing reaction time to several minutes at 400 °C. The released chloride forms calcium chloride (CaCl₂). No toxic chlorinated phenols were produced from this reaction.

Sedlak et al. (1991) studied the alkaline hydrolysis of PCBs using quicklime, CaO, and attempted to discriminate between losses due to degradation and those due to volatilization/temperature effects. They concluded that the temperature of the reaction caused changes in the PCB partitioning between soil-air-water and that no abiotic degradation occurred. In contrast, Weber et al. (2002) and Seok et al. (2005) also examined the alkaline hydrolysis of PCB using flyash and quicklime, respectively, and both reported abiotic degradation. However, both of these efforts required the addition of heat to the reaction (340 °C and 600 °C, respectively) as well as a non-oxygen atmosphere.

The United States Environmental Protection Agency (USEPA) has prepared two reports reviewing treatment technologies, including alkaline hydrolysis, for PCB-contaminated soil, sediments, sludges, and water (Einhaus et al. 1991; Dàvila et al. 1993). In addition, a supplement to the Einhaus report, prepared by Soundararajan (1991), is concerned solely with the alkaline hydrolysis of PCBs. Einhaus et al. (1991) treated three different PCB congeners with quicklime in a closed reaction vessel and recorded a 60 to 80 percent decrease in PCB concentration after 5 hr. The authors concluded that this decrease was due to evaporation and steam stripping from the exothermic reaction, although they found some reaction products. Einhaus' results are contradicted by those of Soundararajan (1991), who attempted to replicate actual site conditions. He found no volatilization of the PCBs, inorganic chloride was present in the final reaction mixture, and the biphenyl ring structure was destroyed. Dàvila et al. (1993) evaluated alternative technologies for treatment of

PCB-contaminated soil and sediment. They divided the treatments by established, demonstrated, and emerging technologies. The use of quicklime (as cement kiln dust) was dismissed as a failed technology.

Polycyclic aromatic hydrocarbons (PAHs)

The PAHs are stable, hydrophobic, and neutral compounds. The arrangement of the rings in some compounds, such as BaP, results in the formation of a "bay" which is the most reactive area on the structure. Chemists use this reactive area to build remediation technologies. Two abiotic technologies currently in use for PAHs are incineration and chemical extraction using a solvent (Federal Remediation Technologies Roundtable (FRTR) 2006). Solvent extraction at pH over 10 is the method used by the BEST™ process at the Grand Calumet (IL) USEPA demonstration site. The organic solvent separates the contaminant from the soil/sediment. The contaminated solvent must then be treated. The solvent will also extract metals, which restricts handling of the residuals. The extraction efficiency is lower for the high molecular weight PAHs and in high clay soils.

Persulfate oxidation

Activated persulfate (peroxydisulfate) is emerging as a cost-effective and viable oxidant for in situ chemical oxidation (ISCO) technology for the treatment of organic contaminants in groundwater, soils, and sediments (Hoag et al. 2000; Huang et al. 2002; Liang et al. 2003; Hoag and Mao 2004). In persulfate chemistry, the chemical oxidation process has a decreased soil oxidant demand and promotes the formation of a variety of free radicals (sulfate free radical SO₄-• and hydroxyl free radical OH•) (Couttenye et al. 2002). It has a relatively high stability under normal subsurface conditions and travels effectively through the subsurface into target contaminant zones (ITRC 2005).

Persulfate activation occurs principally through the formation of sulfate free radicals SO₄-•, following mild thermal (30-100°C) or UV activation of persulfate solutions. These sulfate radicals may initiate a series of radical chain reactions (Berlin 1986), where organic compounds are usually degraded. The radical-generation process may be accelerated at ambient temperature and acidic conditions through the use of transition metal catalysts including iron, copper, silver, manganese, cerium and cobalt (House 1962; Kislenko et al. 1997). The persulfate-ferrous iron catalyzed

reaction is theorized to result in the rapid production of sulfate free radicals (Brown et al. 2002) as described in Figure 10.

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-}$$

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$$

Figure 10. Production of sulfate free radicals from persulfate and catalyzed by ferrous iron.

Non-thermal ISCO using persulfate requires activation by ferrous ions (Hoag et al. 2000) but preferentially chelated metals may be used (Brown et al. 2002; Hoag and Mao 2004; Liang et al. 2004). Chelated iron, for example, has been demonstrated to prolong the activation of persulfate in the pH range 6 to 8. Several practical sources of Fe²⁺ or Fe³⁺ can be considered for activation of persulfate, such as:

- Iron present in the soil minerals that can be leached by injection of a free-chelator (a chelator not complexed with iron, but usually Na⁺ and H⁺),
- Injection of soluble iron as part of a chelate complex, such as Fe(III)-EDTA, Fe(III)-NTA or Fe(III)-citric acid,
- Indigenous dissolved iron resulting from reducing conditions present in the subsurface (common at many sites).

Most of the research performed for remediation of contaminants with persulfate has been targeted toward chlorinated solvents. Prior to using persulfate for this study, two screening tests were conducted to determine the ability of heat-activated persulfate to destroy TNT and PCBs. The results from both tests showed significant destruction of the target compounds.

Explosives

The ITRC (2005) describes explosives as contaminants that are degraded slowly, but are not completely recalcitrant, in the activated persulfate reaction. Hoag and Waisner (2005) and Waisner and Hoag (2006) compared the degradation of TNT by heat-activated persulfate and an iron-chelate-persulfate complex. They reported that the heat activated (40 °C) persulfate completely and rapidly degraded TNT with a first-order kinetic rate of 0.047 mg/L per hour. This oxidation rate is slower than that

reported for either Fenton oxidation (Li et al. 1997b) or alkaline hydrolysis (Felt et al. 2001a). TNT degraded slowly and incompletely when the iron-EDTA complex was added to the reaction mixture. Heat-activated persulfate is a possible ex situ treatment for soil contaminated by explosives.

Polychlorinated biphenyls (PCBs)

The ITRC (2005) describes PCBs as recalcitrant contaminants that are slowly degraded in the activated persulfate reaction. Govindan et al. (2002) set up two laboratory-scale experiments, one combining PCBs in an aqueous persulfate system and another combining PCB-contaminated sediment and persulfate with and without lime. Aqueous experiments run at 40 °C showed a 94 percent decrease in PCB concentration within 56 hr. Slurry experiments (40 °C /50 °C, 12 hr) showed desorption of the PCBs from the soil but no decrease in concentration. Increasing the treatment temperature and time (80 °C, 168 hr) resulted in 95 percent to >99 percent decrease in PCB concentration.

Polycyclic aromatic hydrocarbons (PAHs)

The ITRC (2005) describes PAHs as contaminants that are reluctantly degraded, but not completely recalcitrant, in the activated persulfate reaction. Some of the earliest work with PAHs is described by Peyton et al. (1990), where they report 34 percent reduction in total PAH after 12 days of treatment and 52 percent reduction after 40 days. Marley et al. (2003) compare several ISCO processes, including persulfate, at reducing BTEX and PAH concentrations in soil at a manufactured gas plant. Nadim et al. (2006) added heat and EDTA as a catalyst for persulfate remediation of PAHs in aqueous systems. They reported that persulfate effectively degraded the 16 PAHs targeted by the USEPA to below machine detection limits (MDL) within 144 hr. Preliminary tests run with contaminated soil indicated that persulfate mixed with EDTA-Fe(II) degraded seven PAHs by 70 to 100 percent in 24 hr.

In summary, the scientific literature supports a role for persulfate oxidation as a remediation technology for explosives, PCBs and PAHs.

Fenton's reagent

Fenton's reagent is a mixture of hydrogen peroxide (H₂O₂) and ferrous iron (Fe²⁺). The ferrous iron catalyzes the decomposition of the hydrogen peroxide initiating the formation of the hydroxyl radical (Figure 11). Hydroxyl radicals are very strong, non-specific, oxidizing agents. If the concentrations of the reactants are not rate-limiting, the hydroxyl radical oxidizes organic molecules completely to carbon dioxide and water. The use of Fenton's reagent has been reviewed by Rodgers and Bunce (2001) and Nevens and Baeyens (2003) as well as the ITRC (2005). Various modifications of the basic Fenton reaction include using a higher concentration of peroxide, the use of calcium peroxide, the addition of metal salts as chelating agents, and the use of ultraviolet light. Advantages are that the reaction intermediates are generally more biodegradable and less toxic than the parent compounds. Disadvantages include the possible formation of iron precipitates as part of the reaction. In addition, the low pH can mobilize any metals that are co-contaminants with the organic compounds, potentially contaminating the groundwater. When large concentrations of peroxide are used, the exothermic reaction may result in contaminant volatilization or gas production. The reaction parameters should be evaluated with treatability studies before the technology is used in the field.

The literature supports a role for Fenton's reagent, either in its classic approach or modified by the addition of UV light or zero-valent iron, as a remediation technology for nitroaromatic and nitramine explosives, PCBs, and PAHs.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{-} + HO^{-}$$
 $H_2O_2 + Fe^{3+} \longrightarrow HO_2 + H^{+} + Fe^{2+}$

Figure 11. Fenton's reaction.

Explosives

Fenton's reagent is particularly amenable to the destruction of organic compounds such as TNT, as illustrated in Figure 12 (Neyens and Baeyens 2003; ITRC 2005). Li et al. (1997a, 1997b) studied the reaction parameters of concentration, pH, temperature, and light in soil, soil washings, and

slurries, reporting 2,4,6-trinitrobenzoic acid (TNBA) and 1,3,5-trinitrobenzene (TNB) as products. The initial reaction appeared to be a methyl group oxidation and decarboxylation, followed by nitro group removal, and ring hydroxylation and cleavage. In a second study, Li et al. (1997b) reported that the reaction rate increased with increasing concentrations of fulvic acid. The authors hypothesized that more iron was regenerated at higher fulvic to humic acid ratios. In addition, the reaction rate increased with increasing temperature, when reactants were added sequentially rather than in a single addition, and by the presence of Ca²⁺ - montmorillite clay. Kaolinite, on the other hand, decreased the reaction rate.

Figure 12. Fenton's reaction with organic compounds (from Neyens and Baeyens 2003).

Researchers have also modified the Fenton reaction by

- modifying the iron component
 - using zero-valent iron (Agrawal and Tratnyek 1996; Oh et al. 2003a)
 - o changing the concentration (Liou et al. 2003, 2004)
- adding energy to the reaction in the form of UV light (Celin et al. 2003; Chen et al. 2005; Li et al. 1998)

These changes increase the reaction rate for the destruction of the more recalcitrant organic compounds.

Polychlorinated biphenyls (PCBs)

ITRC (2005) describes the PCBs as contaminants that are reluctantly degraded, but not completely recalcitrant, in the Fenton reaction (H_2O_2/Fe) . The reaction proceeds slowly and is more effective in aqueous systems than in soil/sediment. No case studies were provided for Fenton treatment of PCBs. Sedlak and Andren (1994) examined the reaction pathway and kinetics of Fenton treatment for PCBs in an aqueous system. They determined that the reaction proceeds through the addition of a hydroxyl group to one of the non-halogenated sites on the PCB molecule.

Therefore, as the chlorine content increases, the reaction rate decreases. Within homologues, when the chlorines were in the *meta* and *para* positions, the reaction rate decreased because of the stearic hindrance that results from the hydroxyl attack on the open *ortho* position. McLaughlin et al. (1993) examined the photo-Fenton degradation of two PCBs (IUPAC number 18, 3 chlorine, and IUPAC number 101, 5 chlorine) in a soil system. They found that sorption of the PCB to a soil particle reduces the effectiveness of the Fenton reaction. The PCB must first be desorbed into the aqueous phase for the reaction to proceed.

IT Corporation filed a USEPA Superfund Innovative Technology Evaluation (SITE) report in 1995 describing a bench-scale demonstration that compared the degradation of PCBs and dioxin by UV light alone, Fenton's reagent alone, and a combined UV-Fenton reaction. Each of these treatment systems was followed by a biological degradation step that involved nutrient addition to the soil and bioaugmentation. In the first phase, the authors reported no destruction of the dioxin under UV light treatment alone. In contrast, 23 to 69 percent of PCBs were degraded under UV light treatment. The greatest decrease in concentration occurred in the highly chlorinated PCBs. Under photo-Fenton treatment, 15 to 55 percent of the PCBs were degraded. The highest reduction occurred at the highest Fe:soil ratios and a maximum hydrogen peroxide concentration, up to 2 percent. PCB degradation came more from the lower chlorinated congeners and the degradation results improved at lower soil PCB concentrations.

Polycyclic aromatic hydrocarbons (PAHs)

The ITRC (2005) describes PAHs as contaminants that are slowly degraded, but not completely recalcitrant, in the Fenton reaction (H_2O_2/Fe^{2+}) . They report that the reaction proceeds slowly and is more effective in aqueous systems than in soil/sediment. No case studies were presented for Fenton reaction treatment of PAHs. This information is contradicted by the numerous research reports of successful degradation of PAHs using Fenton oxidation in soil (Sullivan et al. 1982; Kawahara et al. 1995; Engwall et al. 1999; Lindsey and Tarr 2000; Nam et al. 2001; Watts et al. 2002; Flotron et al. 2005; Lundstedt et al. 2006).

Stabilization of lead with phosphate

The ITRC (2003) defines stabilization as a process that uses chemical reagents that react with the contaminants and the soil to form product compounds that have very low solubility and high stability. Historically, it describes several processes by which organic- or metal-bearing wastes could be treated or encapsulated to remove their hazardous characteristic (Cullinane et al. 1986). Stabilization is an established technology that has been used for almost 20 years to treat a variety of wastes at more than 160 Superfund remedial sites throughout the country (USEPA 2001). Because of the formation of nearly insoluble and very robust mineral compounds, stabilized wastes are often considered very protective of groundwater and the environment. The most promising process involves the stabilization of lead in soils by the addition of phosphate material, as many lead phosphate minerals have exceedingly low solubility and high stability (Traina and Laperche 1999; Brown et al. 2004). Many different phosphate reagents have been studied as to their effect on lead solubility in several types of contaminated soils and sediments: phosphoric acid (Yang et al. 2001), calcium hydrogen phosphate and calcium carbonate (Wang et al. 2001), potassium dihydrogen phosphate (Berti and Cunningham 1997), limestone, mineral rock phosphate, and diammonium phosphate (Basta and McGowen 2004), and powdered hydroxyapatite, and calcium, sodium, potassium, and ammonium phosphates Tardy et al. (2003). Several recent studies have also reported that phosphate addition lowered the toxicity of the lead in the contaminated soils, primarily by making it less bioavailable (Yang et al. 2001; Davies et al. 2002; Hettiarachichi et al. 2002; Maenpaa et al. 2002).

2 Experimental Design

Objectives

The goal of this project was to evaluate, using laboratory experiments, treatment approaches for the former PBOW. The project evaluated four chemical treatments for the organic compounds. Stabilization following organic treatment was investigated for treatment of lead.

Design

The conceptual experimental design is outlined in Figure 13. Lime treatment was proposed to treat explosives (TNT and DNT). Lime (hydrated lime, $CaO.H_2O$ or CaH_2O_2) dosing experiments were conducted on slurries composed of the site soils, producing a relationship between lime dose and pH. A target pH of 11 to 11.5 was chosen based on previous work conducted at ERDC (Davis et al. 2007, in press; Davis et al. 2006). The site soil was also sieved, and the soil cobbles were treated by both water and acetonitrile extraction and analyzed for explosives. This established the presence of explosives contamination on both the inner and outer layers of the cobble.

Advanced oxidation was studied as a means to treat residual PCBs and PAHs. Two approaches were investigated: treatment with persulfate and with Fenton's reagent (hydrogen peroxide in the presence of reduced iron). Most of the research performed for remediation of contaminants with persulfate has been targeted toward chlorinated solvents. Prior to using persulfate for this study, two screening tests were conducted to determine the ability of heat-activated persulfate to destroy TNT and PCBs.

Phosphate treatment was investigated for stabilizing lead by the formation of insoluble minerals. Studies conducted by Larson et al. (2007) on stabilizing lead at small arms firing ranges indicate that addition of 3 to 5 percent (w:w) of a commercially available phosphate mineral called Enviroblend® (Premier Chemicals, W. Conshohocken, PA) is very effective under most soil conditions.

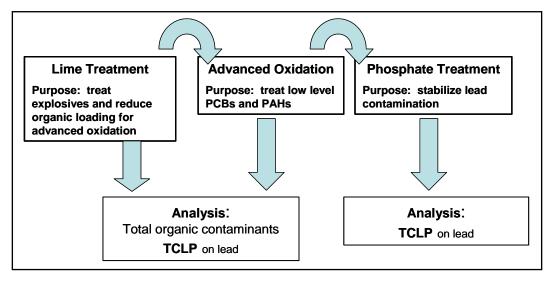


Figure 13. Proposed treatment train for contaminated soil from Plum Brook Ordnance Works.

3 Materials and Methods

Soil preparation

Soils were collected by JEG and received by ERDC in December 2005. The soils were collected from three areas: the deep burn layer, the surface soil of the burn area, and surface soils from west of the burn area. Two 5-gallon buckets were collected from each source area, each from different sites within the source. Soil from each bucket was placed into a separate glass box, which measured 30 in. on each side and 9 in. deep, and allowed to air dry in the laboratory. The soils were spread manually. Large clods of dirt were broken up and clumps of grass were removed, placed in a plastic bag, and kept refrigerated. Steps in the soil processing are illustrated in Figure 14. Each air-dried soil had the rocky material removed and was separated into fractions by sieving through 4.5- and 1.7-mm sieves. Fractions retained on the 4.5- and 1.7-mm sieves were ground. The soil cobbles (>1.77 mm), as shown in Figure 15, were retained from each sample. Half of the cobbles from each sample were ground in a tissue grinder.

Some vegetation is known to sequester metals (Aboulroos et al. 2006; Fischerova et al. 2006; Yoon et al. 2006). In order to obtain a better representation of the actual site remediation, this treatability study included the vegetation found in the sampling zone. The clumps of grass, which were removed earlier, were cut into smaller pieces and then passed through a plant grinder. The resulting ground plant matter was added back to the soil fraction that passed through the 1.7-mm sieve and homogenized in a small cement mixer for a minimum of 30 min. The resulting blended soils were placed back into the same glass boxes used earlier and spread out evenly. Five soil samples (100 g each) were taken from separate locations, the four corners and middle, in each box. The soil samples were then divided and analyzed for moisture content, explosives, PCBs, PAHs, and lead. The values for TNT, DNT, and lead are based on five replicates. The values for Aroclor 1260 (PCB) and benzo(a)pyrene (PAH) are based on three replicates.



A. Plant grinder



B. Unground versus ground material



C. Soil mixers



D. Spread out burn layer

Figure 14. Steps in soil processing.

Analysis methods

Explosives

Extraction and analysis of explosives by high performance liquid chromatography (HPLC) was performed according to USEPA SW846 Method 8330 (1994), modified for soil. Soil samples were extracted by placing 25 g of soil and 25 mL of ACN in a 40-mL amber volatile organic analysis (VOA) vial. Analysis was performed using a DIONEX HPLC system equipped with a C-18 reverse phase column and a photodiode array detector which measured absorbance at 254 nm. The mobile phase was 50/50 (v/v) methanol/organic-free reagent water. The flow rate was set at 1.0 mL/min, and a 25- μ L injection volume was used. The MDL for explosives under these analysis conditions is 0.02 mg/L.



Figure 15. Comparison of cobble material and ground soil.

PCBs

Soils were extracted according to USEPA SW846 Method 3545 (1996). A 15-g sample (wet) was extracted using a Dionex 200 Accelerated Solvent Extractor (ASE) with a solvent ratio of 75/25 (v/v) hexane/acetone. After samples were extracted, the extract was placed in Zymark evaporation tubes in a Zymark Turbo Vap II Concentration Workshop and concentrated to 5 mL. The 5 mL extract was split, half being reserved for PAH analysis. The extract was cleaned according to USEPA Method 3665A (1996) using Mallinckrodt AR Select sulfuric acid, and analyzed according to USEPA Method 8082 (1996) using a Hewlett Packard Series II 5890 Gas Chromatograph equipped with dual electron capture detectors (ECD). The method differentiates 7 Aroclors and 20 individual congeners. The Laboratory Reporting Limit (LRL) for PCBs is 8.33 parts per billion (µg/L).

PAHs

The PCB extract from above was split in half and cleaned on silica gel using USEPA SW846 Method 3630C (1996). The extract was analyzed for

26 different PAHs and various PAH derivatives using a Hewlett Packard 5890 Series II Gas Chromatograph/5971 Series Mass Selective Detector, GC/MSD according to USEPA SW846 Method 8270C for semi-volatile organic compounds (1996).

Metals (lead)

ICP

Soil samples were digested and prepared for analysis using USEPA SW846 Method 3051 (1994) with microwave assistance. Following digestion, liquid samples were filtered using a 0.45-µm syringe filter. A modified USEPA Method 200.7 (1994) was used to analyze liquid samples for soluble concentrations of Pb and phosphorous using the Perkin-Elmer Optima 4300 dual view (DV) inductively coupled plasma (ICP) atomic emission spectroscopy (AES), with a reporting limit of 0.05 mg/L for Pb and 5.0 mg/L for phosphorous. Filtered samples were accompanied by a matrix blank and calibration verification per batch of 20 samples. The acceptance criteria was 90 to 110 percent recovery.

Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP (USEPA SW 846 Method 1311, 1992) was designed to determine the mobility, under specific conditions at a MSW landfill, of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. Each TCLP was performed in triplicate. The TCLP supernatant was filtered using a 0.45-µm syringe filter and analyzed for metals by using the ICP method for liquids.

Statistical analysis

Statistical analysis, primarily ANOVA (confidence interval of 0.95), was performed using the SigmaStat software package, v.3.5 (Systat Software, Inc. (SSI), Richmond, CA). The values for TNT, DNT, and lead are based on five replicates. The values for Aroclor 1260 (PCB) and benzo(a)pyrene (PAH) are based on three replicates.

Lime dosing experiments

Tests were conducted to determine the appropriate dose of hydrated lime (Ca(OH)₂) according to methods published at ERDC (Davis et al. 2007, in press). Lime was added to a soil slurry in doses of 10 to 20 mg until a final

pH of 11 to 11.5 was reached. The total amount of lime added to the soil slurry is used to calculate the amount of lime necessary to either mix into excavated soil of a known volume or to top dress a known soil area to a depth of 3 in.

Slurry experiments

Reactor assembly

Slurry experiments were conducted in one-liter jacketed flasks (Ace Glass number 6523-12, number 6528-35) and stirred with a laboratory mixer (Lightnin TS2010). Soil and water were added at a ratio of 30 percent w/w (soil/slurry). Mixing speed was sufficient to suspend all but a small fraction of the soil in the reactor. The unsuspended fraction appeared to be coarse sand particles. Unheated tests were conducted at a room temperature of approximately 22 °C. In tests requiring heat, water was circulated between a temperature controlled water bath and the water jacket of the flask. The temperature was measured directly in the slurry and the temperature of the water bath was adjusted accordingly (Figure 16). Chemical amendments were added through ports in the top of the reactor.

Slurry samples were collected with 50-mL plastic serological pipettes through ports in the top of the reactor while the slurry was being mixed. Approximately 100 mL of slurry was collected for each sample and placed in two 50-mL glass centrifuge tubes. These tubes were centrifuged at 2,500-g RCF (relative centrifugal force) for 15 min. The pH of the supernatant was measured directly in each tube by a pH electrode. The average of the pH readings from the two tubes was taken to be the pH of the sample. The supernatant from each tube was pipetted by syringe, filtered through a 0.45- μ m glass-fiber syringe filter, and combined in amber glass bottles. All supernatant samples were stored at 5 °C until used for analysis.

Soil remaining in the centrifuge tubes was scraped out with a spatula into an aluminum pan and allowed to air dry in a fume hood. The dried soils were then lightly ground by mortar and pestle and placed in an amber jar. The jar was slowly rolled for 1 min to homogenize the sample. Approximately 5 g of this soil was used for moisture content determination. The remaining soil was stored in the sealed jar at room temperature until used for analysis.



Figure 16. Soil slurry reactor.

Alkaline hydrolysis

In tests with alkaline hydrolysis, two reactors were set up: one for Burn Layer 1 and one for West Surface Soil 2. The mass of lime added was equal to 1.5 percent of the mass of the soil. Samples (both solid and liquid phase) were collected at 0, 1, 3, and 6 days. Supernatant samples from alkaline-hydrolysis tests were neutralized with 300 to 500 μ L of 1.0 N H2SO4.

Lime/persulfate oxidation

Using the 1-L slurry reactors, two 30 percent slurries of burn layer soils were treated with 1.5 percent (w_{lime}/w_{soil}) hydrated lime. One reactor was heated (using the reactor's water jacket) to 40 °C, the second operated at room temperature. Both reactors were initially dosed with lime, and the reaction was allowed to proceed for 24 hr. The reactors were then spiked

with persulfate, to form a 5,000-mg/L concentration of sodium persulfate. The reactors were allowed to run at room temperature for another 6 days. On Day 7 the heated reactor was spiked with persulfate to again form a 5,000-mg/L concentration of sodium persulfate. The unheated reactor was spiked with persulfate and hydrated lime, 5,000 mg/L and 1.5 percent respectively, on Day 7. Samples were collected at 0, 1, 2, 4, 7, and 8 days.

Modified-Fenton oxidation

Additions to the modified-Fenton treatment were included in the following order:

- Fe(III)-EDTA to create a 200-mg/L final aqueous concentration of added iron,
- sufficient concentrated sulfuric acid to reduce the slurry pH to approximately 4, and
- 30 percent H₂O₂ to create a 100-mg/L final aqueous concentration.

Cobble treatment

Cobbles (>1.7 mm), as shown in Figure 15, were extracted in deionized (DI) water (5 g of cobbles to 95 mL of solution). This ratio was chosen since it is identical to a TCLP extraction. Water samples were collected to evaluate leaching. The same cobbles were then extracted with ACN at the same ratio (5 g : 95 mL). Samples were again collected to evaluate leaching. The cobbles were then ground using a standard tissue grinder. The ground cobbles were extracted with ACN using the same ratios.

Phosphate stabilization

EnviroBlend® (Premier Chemicals) is a phosphate based additive used to stabilize lead and other metals in contaminated soils (http://www.enviroblend.com/). Soils from the lime studies were treated with 3 and 5 percent Enviroblend®. In addition, soils from the persulfate study were treated with 3 percent Enviroblend®.

4 Results

Initial contaminant concentrations

Table 6 and Table 7 summarize untreated contaminant levels. Concentration values that exceed the residential PRGs are in italic, boldface type. All of these, except for the Burn Layer 1 DNT concentration, were also above industrial PRGs. The concentration variation is given as relative standard deviation (RSD, standard deviation/average). The values for TNT, DNT, and lead are based on five replicates. The values for PCB (Aroclor 1260) and benzo(a)pyrene (BaP) are based on three replicates. After reviewing the initial concentration results and discussion with JEG, it was agreed that the treatment studies would focus on the burn layer soil (Burn Layer 1) and the west soil (West Surface 2).

Table 6. Initial concentration of organic compounds in untreated soil and the relative standard deviation (%) based on units of mg/kg.

Sample	TNT	DNT ¹	PCB	BaP ²
Burn Area Surface 1	3.71 ± 1.3%	ND	9.98 ± 17.5% ³	0.0085 ± 25%
Burn Area Surface 2	5.61 ± 6.0%	ND	3.65 ± 6.8%	_
West Surface 1	6.48 ± 3.2%	ND	2.87 ± 21.7%	0.0113 ± 39.6%
West Surface 2	14.85 ± 1.6%	1.73 ± 22.4%	2.33 ± 6.0%	_
Burn Layer 1	1548 ± 5.4%	243 ± 7.9%	22.6 ± 21.0%	0.0444 ± 5.7%
Burn Layer 2	237.8 ± 45.6%	70.5 ± 10.5%	1.32 ± 24.1%	_

¹The sum of 2,4- and 2,6-DNT.

Table 7. Initial concentration of lead in untreated soil expressed as both total and leachable lead and the relative standard deviation (%) based on five replicates.

Sample	Total lead	TCLP
Burn Area Surface 1	248 ± 10.8%	135 ± 34.3% ¹
Burn Area Surface 2	333 ± 18.7%	177 ± 4.3%
West Surface 1	241 ± 2.2%	159 ± 5.9%
West Surface 2	211 ± 5.5%	146 ± 10.9%
Burn Layer 1	1189 ± 45.2%	865 ± 7.1%
Burn Layer 2	3306 ± 30.4%	nd

¹Numbers in italic, boldface type exceed the residential PRG. nd = not determined

²Other PAHs were also detected but all were below 0.062 mg/kg, the RPG.

³Numbers in bold, italic type exceed the residential PRG.

Alkaline hydrolysis

Lime dosing experiment

Dosing experiments were conducted on slurries composed of the site soils, producing a relationship between lime dose and pH (Figure 17). In general, the pH response to lime dose was the same for each Plum Brook soil type tested. A target pH of 11 to 11.5 was chosen based on previous work conducted at ERDC. The lime dosing studies with the Plum Brook soils indicated that a lime dose of 1.5 percent w/w (lime/soil) was required in order to achieve this pH.

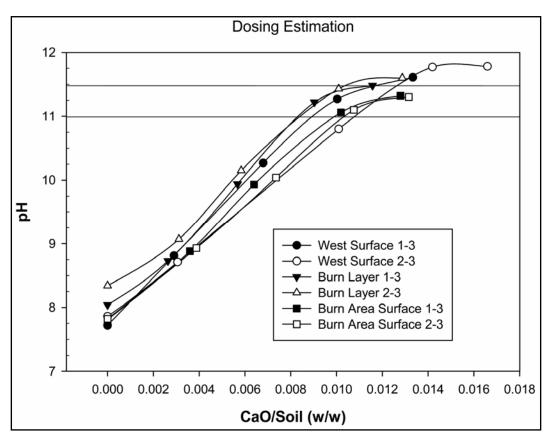


Figure 17. Results of the lime dosing experiment.

Lime slurry experiment

The pH of the solution in the reactors was stable, measuring 10.5 to 11.5 throughout the test. Small amounts of DNT (up to 0.16 mg/L) were found in the reactor solution, but no TNT or PCBs were detected.

The results of soil extraction following alkaline hydrolysis are shown in Figure 18 and Figure 19 for the explosives and PCBs. Removal data for all

compounds are detailed in Table 8. The final values listed in Table 8 for Burn Layer 1 and West Surface Soil 2 are the mean of the final three measurements. These were relatively consistent, in most cases, and were used to provide a good estimate of the final achievable treatment concentration.

The removal of TNT from the burn layer soil was rapid, as can be seen from Figure 18. In the first 24 hr, the concentration decreased from over 1,500 to 93 mg/kg. The final estimated treatment concentration for TNT was 67 mg/kg (96 percent removal), which, however, did not meet either the industrial or the residential PRG of 16 mg/kg (Table 8). The DNTs decreased from 243 to 25 mg/kg in 72 hr, which did meet the residential PRG for both DNTs. PCB levels in Burn Layer Soil 1 decreased about 70 percent, most of which occurred in the first 24 hr. However, the final levels did not meet either the industrial or the residential PRG levels (0.22 mg/kg). Benzo(a)pyrene concentrations (PAH compound) decreased from 0.017 to 0.010 mg/kg, which easily met both the industrial and residential PRGs (0.062 mg/kg).

West Surface Soil 2 had substantially lower levels of contamination. In the case of TNT, the removal rate and percentage were very similar to those in the Burn Layer Soil 1: >90 percent removal of TNT (well below 16 mg/kg, meeting the residential PRG). For the DNTs, the removal was much less (45 percent), but the final concentration met both industrial and residential PRGs. The PCBs were also not treated as successfully, achieving only about 44 percent removal. Even though the initial concentration was much lower than in the burn layer soil, the final concentrations failed to meet the PRGs.

There was no evidence of significant lead loss during the treatment process. A small concentration of lead (144 $\mu g/L$) was found in the reactor solution. Although the lead concentrations in the treated soils were higher than the background measurements, this was due to sample heterogeneity and was within the sample standard deviation.

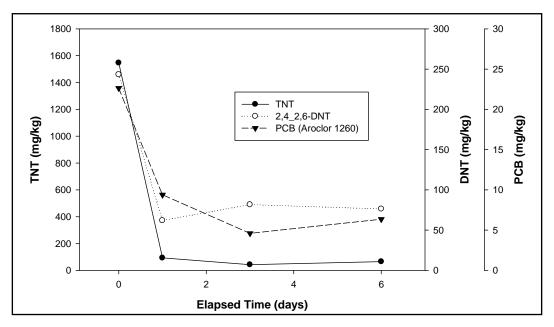


Figure 18. Results of the hydrated lime slurry treatment of Burn Layer Soil 1.

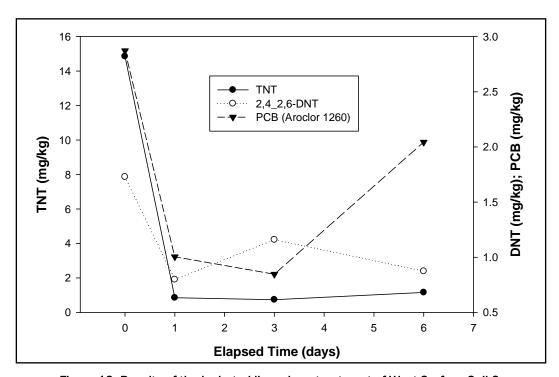


Figure 19. Results of the hydrated lime slurry treatment of West Surface Soil 2.

Soil	Contaminant	Initial (mg/kg)	Final ¹ (mg/kg)	Residential PRG	Industrial PRG
Burn Layer 1	TNT	1547 ± 104	67.3 ± 62.8	N	N
	2,4_2,6-DNT	243.3 ± 23.9	25.30 ± 9.15	Υ	Υ
	PCB (Aroclor 1260)	22.6 ± 11.7	6.78 ± 6.02	N	N
West Surface 2	TNT	14.85 ± 1.59	0.918 ± 0.540	Υ	Υ
	2,4_2,6-DNT	1.728 ± 0.481	0.944 ± 0.472	Υ	Υ
	PCB (Aroclor 1260)	2.33 ± 0.35	1.30 ± 1.62	N	N
¹Values are mean ± 95 percent confidence interval.					

Table 8. Removal of organic compounds by alkaline hydrolysis.

Persulfate oxidation

Contaminant removal resulting from the persulfate treatment at 40 °C is shown in Figure 20 and Figure 21 for the burn layer and the west surface soils, respectively. The results are detailed in Table 9. The final values listed are the mean of the final three measurements. These were relatively consistent and were used to provide a good estimate of the final achievable treatment concentration. Most of the contaminant removal occurred within the first 24 hr of treatment, with steady, modest removal continuing through the remaining experimental period. Small amounts of TNT and DNT were found in the reactor solution. However, the majority of the contaminant mass remained in the soil and was either degraded or transformed. As in the lime slurry experiment (alkaline hydrolysis), only a low concentration of lead was detected in the reactor solution (58 $\mu g/L$). Because the lead concentration in the soil did not change substantially, the authors concluded that lead mobilization was minimal.

Persulfate in the solution was consumed quickly, declining from 5,000 to 143 mg/L in 24 hr. This decrease was unexpected, as most published work indicates that persulfate is very stable in the subsurface environment. Burn Layer Soil 1 contained approximately 20,000, 200, and 100 mg/kg of total iron, manganese, and copper, respectively. These transition metals can be used to catalyze persulfate reactions, and their presence in high concentration is a possible cause of the rapid persulfate consumption. The rate of persulfate consumption appears to be significantly slower in the West Surface Soil 2. The concentrations of transition metals were also significantly lower than that seen in Burn Layer Soil 1: approximately 1,700 mg/kg for manganese and 20 mg/kg each of iron and copper.

Persulfate treatment of the burn layer soil demonstrated >80 percent removal of TNT and the PCB Aroclor 1260, but only 39 percent removal of DNTs. Despite these high removal rates, TNT and the PCBs did not meet either the residential or the industrial PRG. DNT met the industrial but not the residential PRG. Treatment of the west soil, even with its much lower initial concentrations, did not perform as well. TNT and the PCBs amounted to only 69 percent and 11 percent removal, respectively. The DNTs had no significant change in concentration. However, due to those lower initial concentrations, the decreases were great enough to allow TNT and the DNTs to reach both the residential and industrial PRGs.

Lime/persulfate oxidation

Discussion

Contaminant removal from the lime-persulfate slurry reactors is shown in Figure 22 and Figure 23 for Burn Soil 1 treated at 25 °C and 40 °C, respectively. Results were similar for both temperatures. A pH of 12 was recorded after the introduction of hydrated lime into the reactor. This was accompanied by rapid removal of the organic contaminants. After the addition of the persulfate (Day 1), the pH of the slurry dropped to below 9. Beginning at Day 1, with the decrease in pH, removal of TNT and DNT appears to have ceased and concentrations remained steady throughout the remainder of the experiment. However, the concentration of PCBs in the soil appears to have decreased until Day 2 after which it remained relatively constant. The slurry was re-spiked with both lime and persulfate at Day 7, but no further degradation of the contaminants was apparent.

Literature review found (as discussed earlier in this report) that a pH over 11 for an extended reaction period is required for the alkaline hydrolysis of the DNTs, and over 10.5 for TNT. The data indicate a continuing consumption of the hydroxide ion as well as a loss of persulfate. Low concentrations of TNT and the DNTs were measured in the slurry solution during the reaction period. These are shown in Table 10.

The final concentrations of TNT, the DNTs, and PCB-Aroclor 1260 detailed in Table 11 are the mean of the final three measurements. These were relatively consistent and were used to provide a good estimate of the final achievable treatment concentration. The lime-persulfate at 25 °C resulted in 92 percent removal of the TNT. The DNTs and PCB achieved 56 percent and 73 percent removal, respectively. The same experiment run

at 40 °C resulted in similar contaminant removals, 92 percent, 44 percent, and 72 percent for TNT, DNTs and PCB, respectively. From these data, the conclusion is that elevated temperatures do not increase contaminant degradation in this remediation system.

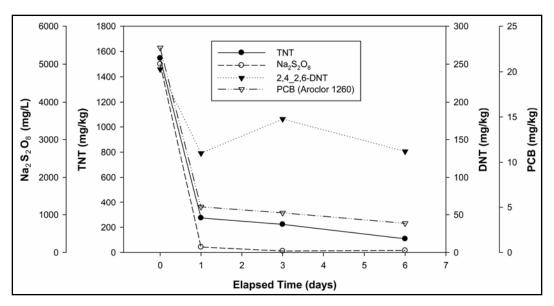


Figure 20. Results of persulfate slurry treatment of Burn Layer Soil 1 at 40 °C.

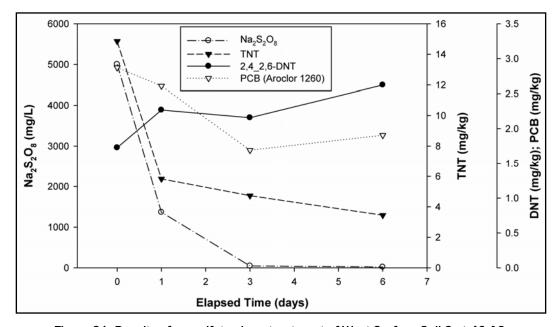


Figure 21. Results of persulfate slurry treatment of West Surface Soil 2 at 40 °C.

Table 9. Removal of	f organic compo	unds by thermall	v activated	persulfate (40 °C	۲).

Treatment	Compound	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Residential PRG	Industrial PRG
Burn layer, 5,000 mg/L,	TNT	1547 ± 104	202 ± 211	N	N
40 °C, 6 days	DNTs	243.3 ± 23.9	147.8 ± 63.1	N	Υ
	PCBs	22.6 ± 11.7	4.21 ± 2.29	N	N
West soil, 5,000 mg/L,	TNT	14.85 ± 1.59	4.67 ± 2.96	Υ	Υ
40 °C	DNTs	1.728 ± 0.481	2.35 ± 0.61	Υ	Υ
	PCBs	2.33 ± 0.35	2.07 ± 1.19	N	N

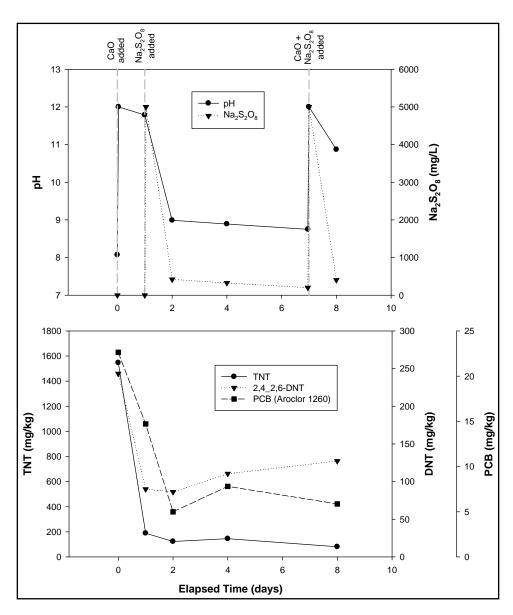


Figure 22. Removal of organic compounds from Burn Layer Soil 1 through a combination of alkaline hydrolysis and persulfate oxidation at 25 °C.

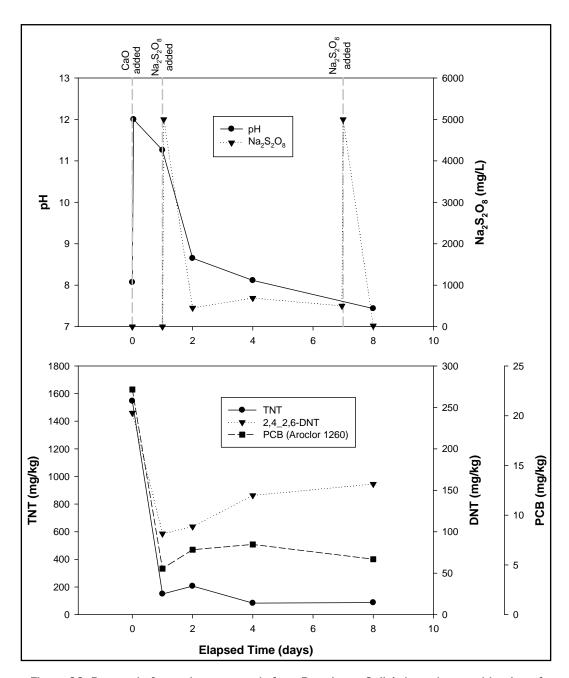


Figure 23. Removal of organic compounds from Burn Layer Soil 1 through a combination of alkaline hydrolysis and persulfate oxidation at 40 °C.

Table 10. Concentration of explosives found in solution during the combined alkaline hydrolysis/persulfate oxidation of burn layer soil.

Sample Time (days)	TNT (mg/L)	DNTs (mg/L)
0	0	0
1	0.09	0.16
2	0.30	0.18
4	0.23	0.19
7	0.01	0.27

Table 11. Effect of experimental conditions on lime hydrolysis/persulfate oxidation of burn layer soil.

Treatment	Compound	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Residential PRG	Industrial PRG
Lime/persulfate	TNT	1547 ± 104	117 ± 81	N	N
25 °C	DNTs (total)	243.3 ± 23.9	108 ± 51	Y	Υ
	PCBs	22.6 ± 11.7	6.21 ± 3.59	N	N
Lime/persulfate 40 °C	TNT	1547 ± 104	125 ± 174	N	N
	DNT (total)	243.3 ± 23.9	136 ± 66	N	Υ
	PCBs	22.6 ± 11.7	6.38 ± 1.87	N	N

Comparison of treatment variation on contaminant removal

A comparison of the final concentrations resulting from the various treatments is illustrated in Figure 24, Figure 25, and Figure 26 for TNT, the DNTs, and PCB-Aroclor 1260, respectively. The treatments are alkaline hydrolysis (AH), persulfate oxidation at 40 °C (P40), alkaline hydrolysis followed by persulfate oxidation (AH-P), and alkaline hydrolysis followed by persufate oxidation at 40 °C (AH-P40). In summary, an analysis of variance indicated that only the DNTs were removed to a significantly lower concentration (95 percent confidence) by one of the treatments, and that was alkaline hydrolysis alone.

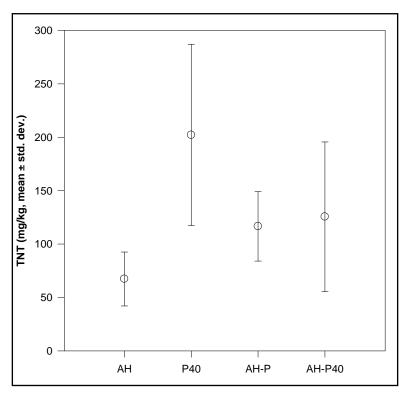


Figure 24. Final concentration of TNT in Burn Layer Soil 1 after each treatment.

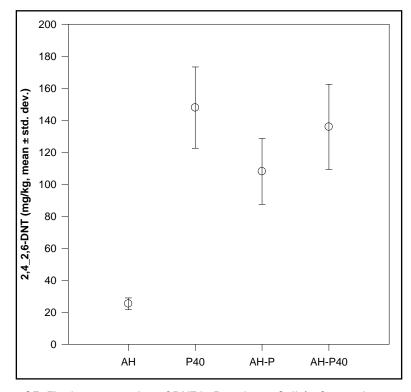


Figure 25. Final concentration of DNT in Burn Layer Soil 1 after each treatment.

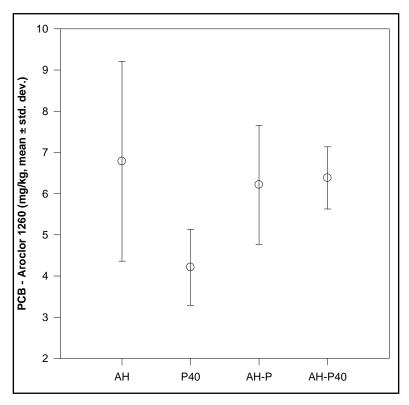


Figure 26. Final concentration of PCB-Aroclor 1260 in Burn Layer Soil 1 after each treatment.

Modified-Fenton oxidation

The reaction associated with Fenton's chemistry was extremely fast and potentially violent. Figure 27 illustrates temperatures collected over a 62-min period following the startup of the reactor. Within 15 min, temperatures had reached 95 °C. The reactor was shut down after 62 min of operation, but it is likely that the bulk of the reactions occurred in the 15-min period of temperature increase. About 85.1 percent of the TNT, 43.2 percent of the DNTs, and 78.4 percent of the PCBs were removed while the temperature was increasing (Table 12). Of these, only the DNTs met the industrial PRGs, but the extent of removal of all the contaminants was substantial considering the short reaction time. Because the technology did not meet the goals for remediation of the organic compounds, the authors did not test for lead in the reactor solution or soil.

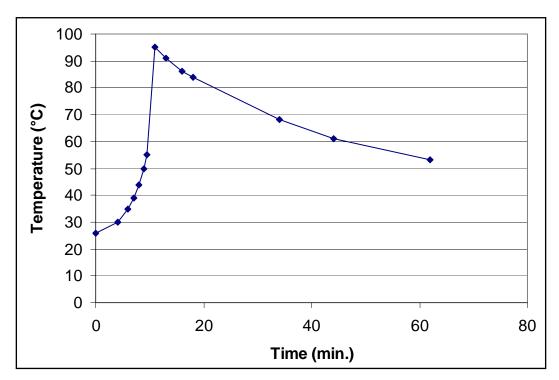


Figure 27. Temperature profile of Fenton reaction during treatment of PBOW soil.

Compound	Final Concentration (mg/kg)	Removal (%)	Residential PRG	Industrial PRG
TNT	231	85.0	N	N
DNT	138	43.2	N	Υ
PCBs	4.9	78.4	N	N

Table 12. Results of Fenton oxidation of PBOW burn layer soil.

The experimental effort for this approach was preliminary, as it would be possible to test sequential reactions or higher peroxide doses. However, the speed of the Fenton's reaction is counterbalanced by the high volatility of the reaction, which may result in explosive reactions if not properly managed. Given the high levels of transition metals previously mentioned in the persulfate oxidation results, it is likely that any addition of hydrogen peroxide will result in a very rapid reaction with these transition metals, and sequential low-level doses of hydrogen peroxide would be necessary in the field for safe application. Although peroxide is not prohibitively expensive, it is more difficult to manage than lime or persulfate. These safety and operational concerns led the authors to focus their efforts on alternative approaches.

Cobble treatment

The DI extraction indicated that soluble explosives were present in the cobbles (Figure 28). The subsequent ACN extraction was substantially higher than the water. This suggests that water washing will be inefficient for dealing with the cobble material. Explosives concentrations from the ground cobbles were slightly lower than that of the whole material. This suggests that the cobbles do not shield significant levels of explosives in their core.

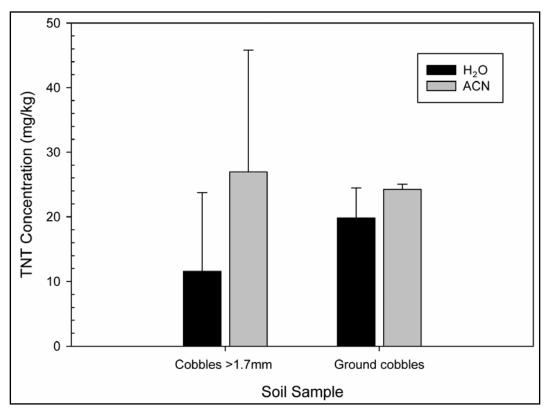


Figure 28. Comparison of explosives concentrations from solid and ground cobbles by water and solvent extraction.

Phosphate stabilization

As seen in Figure 29, treatment with both the 3 percent and 5 percent EnviroBlend® significantly decreased the TCLP extraction of the limetreated soil. Both treatments were below the TCLP standard for lead (5 mg/L). Similar results were obtained with the persulfate-treated soil.

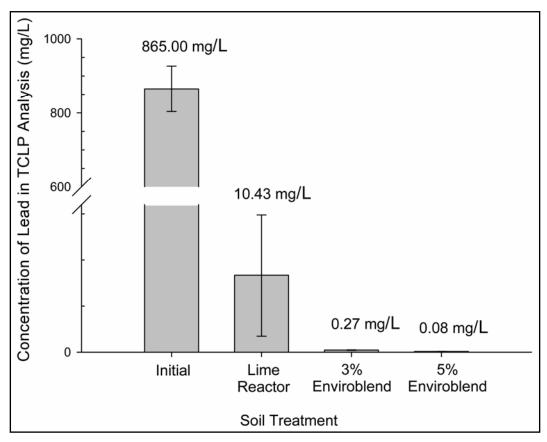


Figure 29. TCLP for lead following phosphate stabilization of lime-treated soil.

5 Discussion

Comparison of alkaline hydrolysis and persulfate oxidation

Figures 24, 25, and 26 compared the various treatments examined for removal of contaminants from PBOW burn layer soil. They indicate that removal of TNT and of PCBs by lime, persulfate, and by lime/persulfate were very similar in terms of final concentrations.

Contaminant removal from soils is often limited in rate and extent by contaminant solubility and adsorptive properties. The actual transformation or destruction of the contaminants in these chemical treatments occurs only after the contaminant is desorbed into the liquid phase. Desorption rate is dependent on the gradient between the contaminant in the liquid phase and in the solid phase. As treatment proceeds, the soil concentration decreases, reducing the driving mechanism for desorption, and reducing treatment in the liquid phase.

Reaction rates can affect desorption rates because as the contaminant is degraded, it allows for more contaminant transfer into the solution. In general, if the rate of desorption is higher than the reaction rate, the removal rate (in the soil) will be controlled by the reaction rate. On the other hand, if the reaction rate is higher than that of the desorption rate, the removal rate will be controlled by the desorption rate. Further, some fraction, usually small, of the contaminant may be bound at a higher energy, and the corresponding rate of desorption may be very slow compared to the majority of the adsorbed contaminant. This fraction of the contaminant is typically not treatable without thermal desorption.

This study suggests that contaminant desorption, particularly for TNT and PCBs, controlled their removal rate from the slurry reactors. First, the similarities of the removal profiles for the burn layer indicate that a common factor controlled the reactions. The reaction rates of the various treatments would not be expected to be the same. However, the desorptive characteristics would likely be very similar for each treatment, barring any surfactant type interactions with the specific treatment agents. Further, analysis of the reaction solutions indicated non-detect of TNT and PCBs or very low levels. This supports the hypothesis that the destructive reactions were fast compared to the contaminant desorption.

In addition, desorption appears to have a role in the final removal level of the contaminants for the various treatments. This was particularly true for PCBs, which had a final concentration range of 4.2 to 6.8 mg/kg (Figure 26). There was more variability in the final TNT ranges, from 67 to 231 mg/kg (Figure 24).

Alkaline hydrolysis of PCBs

Previous studies have indicated that heat generated by quicklime can volatilize PCBs (Einhaus et al. 1991). As our studies used hydrated lime, heat generation was minimal. Therefore, the removal of the PCBs by our lime treatment was unexpected. This favorable result was replicated in all three of our tests. The authors proposed a second treatment by persulfate specifically to remove the PCBs. In fact, the removal by lime was close to that achieved by persulfate treatment.

Four treatments were conducted involving lime: lime treatment of burn layer soil, lime treatment of west soil, and two lime treatments followed by persulfate treatment of burn layer material. In the four treatments involving burn layer soil, the removal of PCBs was consistent from experiment to experiment. Removal was also found in the west soil study. The experiments were conducted in closed glass reactors, but they did not have air-tight seals. Aggressive exothermic reactions will result in leakage. This was noticed in the Fenton's reagent test where the temperature exceeded 90 °C. Exothermic reactions were not observed in the lime treatment studies due to the use of hydrated (agricultural) lime. Further removal of the PCBs in the lime treatment was not "instantaneous," rather it involved intermediate removal steps.

The study documented in Einhaus et al. (1991) disputes the effectiveness of lime treatment for PCBs. Instead, they attributed removal primarily to thermal desorption. They also suggest that some reported removal may be the result of faulty extractions and analysis. Regarding volatilization, there are key differences in this study versus the Einhaus study, particularly in the type of lime used (this study using hydrated), the amount of lime added (>200 percent vs. 1.5 percent), the age of the soil/contaminant mixture (freshly added congeners vs. aged field soils) and concentration of the PCBs (>3,000 mg/kg vs. ~20 mg/kg), and maximum treatment temperatures (~100 °C vs. 25 °C). These differences make the Eihaus et al. conclusions regarding thermal removal inappropriate for this study.

Regarding issues with extraction and analysis, the extraction procedure (Accelerated Solvent Extraction) used in this study appears to be at least as effective as the Soxlet extraction procedures used in Einhaus et al. (1991). The chromatograms were visually inspected for any obvious shifts in peak locations and no evidence was found. The quality assurance steps, such as check standards and calibration blanks, were within acceptable parameters throughout the test. Therefore, the authors conclude that false results due to extraction and analysis issues are unlikely. A literature review has identified a number of reports and refereed papers that describe alkaline hydrolysis reactions of PCBs (Brunelle and Singleton 1985; Brunelle et al. 1985). Although many of these involve elevated temperatures (Weber et al. 2002; Seok et al. 2005), there are several that describe reactions at ambient conditions (Payne et al. 1991; Soundararajan 1991). Even the Einhaus study documented transformation products from lime reaction.

A troublesome detail is that although there were numerous differences between this study and Einhaus's study, if this study does indicate lime removal of PCBs, then at least some removal of this nature would be expected in their study as well. Upon review of their data, there might be some evidence of this occurring. Figure 3 in Einhaus et al. (1991) is a graph showing PCB removal in a quicklime treated soil. Data collected at 5 hr indicates a large decrease in PCB concentration, presumably due to thermal removal during the slaking process. However, data from 5 to 72 hr indicates continuing PCB removal. They attribute this to continuing thermal removal. An alternative explanation might be an alkaline hydrolysis reaction. Einhaus indicates that buildup of PCB degradation intermediates was minimal and did not account for the amount of PCBs removed. However, if the intermediates were degraded themselves, this pattern would not be unexpected.

In summary, although these authors did not meet the PRGs set as goals for this site, this study does suggest that alkaline reactions may result in substantial removal of PCBs under the right conditions. This mechanism may be effective for PCB treatment in some cases. However, more studies on the ultimate fate of the PCBs, including identification of breakdown products, are needed.

Potential of Fenton oxidation

Fenton's treatment involves reactions with hydrogen peroxide and iron to create highly reactive oxidizing radicals, particularly the hydroxide radical. This study indicated that Fenton's oxidation rapidly removed TNT, DNT, and PCBs, though the removal was not as efficient as the lime treatment. However, based on the temperature profile in Figure 27, it is clear that the actual reaction time was on the order of 15 min. It is likely that sequential treatment would have resulted in much better results, probably on the order of those found for the other treatment processes. In fact, the Fenton's treatment might be able to achieve better results due to the heating processes involved. The heat created by the reaction might allow for greater contaminant desorption, resulting in more efficient treatment.

The challenge of Fenton's application is the explosiveness of the reaction. The reaction process blew out plugs in the reactor ports and resulted in some loss of the solution. Any application of this approach must allow for appropriate venting and heat dissipation. Still, for applications that require rapid treatment, Fenton's would be worth investigating.

Lead co-contamination

Treatment of the soil was further complicated by the presence of lead contamination. There are few reports in the literature of treatments handling co-contamination with organics and heavy metals. Cline et al. (1994) attempted soil washing with limited success. Electrokinetics has been used with some success by Maturi and Reddy (2006) and Wang et al. (2007). Maturi and Reddy used cyclodextrin-assisted electrokinetics to study the transport of nickel and phenanthrene in kaolin. One pore volume of flushing resulted in the removal of 50 percent of the phenanthrene. In all tests, nickel moved quickly to the cathode and precipitated as Ni(OH)₂. Electrokinetics employed in an upward mode was used to remediate kaolin contaminated with copper, lead, xylene, and phenanthrene. The organic compounds required operating conditions substantially different than those for heavy metals. In 6 days of treatment they achieved removal efficiencies of 67 percent, 93 percent, 62 percent, and 35 percent for phenanthrene, xylene, copper, and lead, respectively. Co-contamination remains a difficult scientific and engineering issue in remediation.

Previous experience by these authors with lead contamination in soil from small arms firing ranges led us to focus on phosphate stabilization (with EnviroBlend®), as opposed to removal, which seldom meets treatment standards (Larson et al. 2007). EnviroBlend®, being a mineral form of phosphate, should be more stable than biological forms of phosphate over the long-term of remediation. EnviroBlend® has been used successfully to treat over 3 million tons of contaminated media at sites ranging in size from 50 to 400,000 cu yd under diverse physical settings requiring a wide variety of equipment (http://www.enviroblend.com). Because the slurry reactors would likely remove the stabilization agent, in this case phosphate, the lead was stabilized last in the treatment process. The concern was that the initial treatment processes would solubilize the lead and the solutions used in the slurry reactors would have to be treated for metals contamination.

Lime treatment, which the authors determined would be critical for removal of the explosives in the soils, would have pH levels over 10. As discussed in the introduction, lead is amphoteric, and its solubility increases at high pH, therefore lead leachability was a great concern. Lead was found in the reactor solutions. However, the concentrations were small (144 μ g/L for lime treatment, similar levels for persulfate and lime/persulfate treatments), well below RCRA standards as a hazardous waste (5 mg/L), but above USEPA drinking water action levels of 15 μ g/L (USEPA 2004) (*www.epa.gov/safewater/mcl.html#mcls*). The reaction water would require controlled management, but would not be a hazardous waste and could be reused in subsequent treatment batches. The lead concentrations in the soils did not decrease, indicating that lead removal during organic treatment was insignificant.

Phosphate treatment of the soils that had previously undergone lime treatment indicated very effective stabilization of the lead. This would allow for disposal of lead contaminated soils as a non-hazardous waste and even managed onsite. However, due to safety concerns (ingestion by small children), return of the lead contaminated soils for unrestricted residential use may not be possible. Therefore, these soils would have to be landfilled.

Field application

Figure 30 is a schematic demonstrating how the authors expect this approach to be used in the field. First, the soil will be excavated and then staged for treatment. The material would be screened, and cobbles will

either be ground before going through the treatment system or placed in a landfill. The soils will be batch-treated in a slurry reactor (such as in a cement mixer truck). The resultant material will be placed in a landfill, disposed onsite, or recycled onsite (such as in asphalt for road construction or fill).

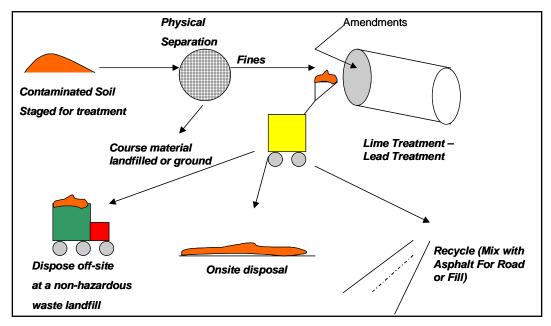


Figure 30. Schematic of conceptual field application.

6 Conclusions

Based on the experiments presented above, the following conclusions can be drawn:

- The treatments (lime, persulfate, and lime/persulfate) are all capable of >90 percent reduction of TNT. The final treatment levels for the burn layer were close to the PRGs, in some cases lower, in other cases slightly higher. Treatment of the west soil easily met the industrial and residential PRG.
- Removal of DNT was not as effective as removal of TNT. However, the removal by lime treatment was sufficient to meet the industrial PRG, even for the burn layer, and often the residential level as well.
- All the treatments resulted in >80 percent reduction of PCBs.
 However, no treatment was able to meet the industrial PRG for the samples tested.
- Benzo(a)pyrene had modest concentration decreases as the result of treatment. The concentrations were below the PRG for this contaminant. However, it is not clear if the treatments would be effective for treating soils that exceed the PRGs, which have been found in the contaminated area.
- The treatment solutions had low, but detectable, concentrations of TNT, DNT, and lead, but no detectable PCBs. There was evidence of removal of the explosives over time, but the authors were not able to experimentally confirm whether this would reach non-detect levels.
- Overall, the lime and persulfate treatment did not appear to substantially affect the lead concentrations in the soils. Lime treatment, in fact, substantially decreased the lead extracted by TCLP, although lead still did not meet the 5 mg/L RCRA standard.
- The phosphate treatments using Enviroblend® easily met TCLP standards.

References

Aboulroos, S. A., M. I. D. Helal, and M. M. Kamel. 2006. Remediation of Pb and Cd polluted soils using in situ immobilization and phytoextraction. *Soil Sed. Contamin.* 15: 199-215.

- Agency for Toxic Substances and Disease Registry (ATSDR). 1995. *Toxicological profile for 2,4,6-trinitrotoluene (TNT)*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2000. *Toxicological profile for polychlorinated biphenyls (PCBs)*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2001. *Toxicological profile for polycyclic aromatic hydrocarbons*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2005. *Toxicological profile for lead.* Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Agrawal, A., and P. G. Tratnyek. 1996. Reduction of nitroaromatic compounds by zero-valent iron metal. *Environ. Sci. Technol.* 30: 153-160.
- Alexander, R. R., and M. Alexander. 2000. Bioavailability of genotoxic compounds in soils. *Environ. Sci. Technol.* 34: 1589-1593.
- Arienzo, M. 1999. Decontamination of TNT-polluted water by modified Fenton reagent. *Bioremediation of Nitroaromatic and Haloaromatic Compounds* 5(7): 197-202, Battelle Symposium, Alleman and Leeson (ed).
- Basta, N. T., and S. L. McGowen. 2004. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. *Environ. Pollution.* 127: 73-82.
- Berlin, A. A. 1986. Kinetics of radical-chain decomposition of persulfate in aqueous solutions of organic compounds. *Kinetics and Catalysis* 27(1): 34-39.
- Berti, W. R., and S. D. Cunningham. 1997. In-place inactivation of Pb in Pb-contaminated soils. *Environ. Sci. Technol.* 31: 1359-1364.
- Bogan, B. W., and W. R. Sullivan. 2003. Physiochemical soil parameters affecting sequestration and mycobacterial biodegradation of polycyclic aromatic hydrocarbons in soil. *Chemosphere* 52: 1717-1726.
- Brannon, J. M., and J. C. Pennington. 2002. *Environmental fate and transport process descriptors for explosives*. ERDC/EL TR-02-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Brown, S. L., R. L. Chaney, J. Hallfrisch, J. A. Ryan, and W. R. Berti. 2004. In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc and cadmium. *J. Environ. Qual.* 33: 522-531.

- Brown, R., D. D. Robinson, D. Sethi, and P. Block. 2002. Second generation persulfate ISCO. Second International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, 17 Nov 2002, Toronto, Canada.
- Brunelle, D. J., A. K. Mendiratta, and D. A. Singleton. 1985. Reaction/removal of polychlorinated biphenyls from transformer oil: Treatment of contaminated oil with poly(ethylene glycol)/KOH. *Environ. Sci. Technol.* 19(8): 740-746.
- Brunelle, D. J., and D. A. Singleton. 1985. Chemical reaction of polychlorinated biphenyls on soils with poly(ethylene glycol)/KOH. *Chemosphere* 14(2): 173-181.
- Celin, S. M., M. Pandit, J. C. Kapoor, and R. K. Sharma. 2003. Studies on photodegradation of 2,4-dinitrotoluene in aqueous phase. *Chemosphere* 53: 63-69.
- Chen, W-S., C-N. Juan, and K-M. Wei. 2005. Mineralization of dinitrotoluenes and trinitrotoluene of spent acid in toluene nitration process by Fenton oxidation. *Chemosphere* 60(8): 1072-1079.
- Cline, S. R., B. E. Reed, and M. R. Matsumto. 1994. Efficiencies of soil washing solutions for remediation of lead and organically contaminated soils. In *Proceedings of the Industrial Waste Conference*, West Lafayette, Indiana, United States, 10-12 May 2003, 48: 169-177.
- Couttenye, R. A., K-C. Huang, G. E. Hoag, and S. L. Suib. 2002. Evidence of sulfate free radical (SO₄-*) formation under heat-assisted persulfate oxidation of MTBE. *Proceedings of the 19th Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Assessment, and Remediation*, Conference and Exposition, Atlanta, GA, United States, 5-8 Nov 2002, 345-350.
- Cullinane, M. J., L. W. Jones, and P. G. Malone. 1986. *Handbook for stabilization/solidification of hazardous waste*. EPA/540/2-86-001. Cincinnati, OH: U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory.
- Davies, N. A., M. E. Hodson, and S. Black. 2002. Changes in toxicity and bioavailability of lead in contaminated soils to the earthworm *Eisenia fetida* (Savigny 1826) after bone meal amendments to the soil. *Environ. Toxicol. Chem.* 21: 2685-2691.
- Dàvila, B., K. W. Whitford, and E. S. Saylor. 1993. *Technology alternatives for the remediation of PCB-contaminated soil and sediment*. EPA/540/S-93/506. Cincinnati, OH: U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory.
- Davis, J. L., M. C. Brooks, S. L. Larson, C. C. Nestler, and D. R. Felt. 2006. Lime treatment of explosives-contaminated soil from munitions plants and firing ranges. *Soil Sed. Contamin.* 15(6): 565-580.

Davis, J. L., S. L. Larson, D. R. Felt, C. C. Nestler, M. L. Riggs, W. A. Martin, E. J. Valente, and G. R. Bishop. 2007. *Engineering consideration for hydroxide treatment of training ranges*. ERDC TR-07-7. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

- Einhaus, R. L., I. Honarkhah, and P. Erickson. 1991. *Fate of polychlorinated biphenyls* (*PCBs*) in soil following stabilization with quicklime. USEPA 600/2-91/052. Cincinnati, OH: Risk Reduction Engineering Laboratory.
- Emmrich, M. 1999. Kinetics of the alkaline hydrolysis of 2,4,6-trinitrotoluene in aqueous solution and highly contaminated soils. *Environ. Sci. Technol.* 33(21): 3802-3805.
- Emmrich, M. 2001. Kinetics of the alkaline hydrolysis of important nitroaromatic cocontaminants of 2,4,6-trinitrotoluene in highly contaminated soils. *Environ. Sci. Technol.* 35(5): 874-877.
- Engwall, M. A., J. J. Pignatello, and D. Grasso. 1999. Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-Fenton reaction. *Wat. Res.* 33(5): 1151-1158.
- Federal Remediation Technologies Roundtable (FRTR). 2006. Available on-line at www.frtr.gov
- Felt, D. R., S. L. Larson, and L. D. Hansen. 2001a. *Kinetics of base-catalyzed 2,4,6-trinitrotoluene transformation*. ERDC/EL-TR-01-17. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Felt, D. R., S. L. Larson, and L. D. Hansen. 2001b. *The molecular weight distribution of the final products of the TNT-hydroxide reaction*. ERDC/EL TR-01-142. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Felt, D. R., S. L. Larson, and E. J. Valente. 2002. UV-VIS spectroscopy of 2,4,6-trintrotoluene-hydroxide reaction. *Chemosphere* 49: 287-295.
- Fischerová, Z., P. Tlustoš, J. Száková, and K. Šichorová. 2006. A comparison of phytoremediation capability of selected plant species for given trace elements. *Environ. Pollut.* 144: 93-100.
- Flotron, V., C. Delteil, Y. Padellec, and V. Camel. 2005. Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process. *Chemosphere* 59(10): 1427-1437.
- Govindan, S. V., G. E. Hoag, and K.-C. Huang. 2002. Treatment of PCB contaminated sediment by persulfate oxidation with pozzolanic reaction. *Proceedings of the 18th Annual International Conference on Contaminated Soils, Sediments, and Water*. University of Massachusetts at Amherst, Amherst, MA, 17-19 October 2002.
- Hansen, L. D., D. D. Ringelberg, D. R. Felt, and J. Davis. 2001. *Base-catalyzed 2,4,6-trinitrotoluene transformation. Titration studies.* ERDC/EL TR-01-222. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Hansen, L. D., S. L. Larson, J. L. Davis, C. C. Nestler, and D. R. Felt. 2003. *Lime treatment of 2,4,6-trinitrotoluene contaminated soils: Proof of concept study*.
 ERDC/EL TR-03-15. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

- Hettiarachichi, G. M., G. M. Pierzynski, and M. D. Ransom. 2002. In situ stabilization of soil lead using phosphorus and manganese oxide. *Environ. Sci. Technol.* 34: 4614-4619.
- Hoag, G., P. Chheda, B. Woody, and G. Dobbs. 2000. Chemical Oxidation of Volatile Organic Compounds. U.S. Patent No. 6,019,548, Issued Feb. 1, 2000.
- Hoag, G., and F. Mao. 2004. Iron chelate activated persulfate oxidation: Reactions and mechanisms. *Proceedings of the Third International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater (ORTs-3)*. San Diego, CA, October 24-28, 2004.
- Hoag, G., and S. A. Waisner. 2005. Oxidation of TNT, HMX and RDX by iron-chelate activated persulfate. *Proceedings of the 21st International Conference on Soils, Sediments, and Water.* Amherst, MA: University of Massachusetts at Amherst, October 17-20, 2005.
- House, D. A. 1962. Kinetics and mechanisms of oxidations by peroxydisulfate. *Chem. Revs.* 62: 185-203.
- Huang, K., R. A. Couttenye, and G. Hoag. 2002. Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). *Chemosphere* 49(4): 413-420.
- Hutzinger, O., S. Safe, and V. Zitko. 1974. *The chemistry of PCB's.* Cleveland, OH: CRC Press.
- Interstate Technology and Regulatory Council (ITRC). 2003. Characterization and remediation of soils at closed small arms firing ranges. SMART-1. Washington, DC: ITRC, Small Arms Firing Range Team. http://www.itrcweb.org.
- Interstate Technology and Regulatory Council (ITRC). 2005. Technical and regulatory guidance for in situ chemical oxidation of contaminated soil and groundwater. 2nd ed. In Situ Chemical Oxidation Team. http://www.itrcweb.org.
- Jacobs Engineering Group, Inc. (JEG). 2006. *Engineering evaluation/cost analysis* (EE/CA) for contaminated soil at Reservoir No. 2 Burning Ground (2BG) at the former Plum Brook Ordnance Works (PBOW). U.S. Army Corps of Engineers, Huntington District (CELRH), Contract DACW62-03-D-0004.
- Janowsky, J. V. 1891. Ueber eine reaction der dinitrokörper. Berichte 24: 971.
- Karasch, C., M. Popovic, M. Qasim, and R. K. Bajpai. 2002. Alkali hydrolysis of trinitrotoluene. *Appl. Biochem. Biotechnol.* 98(1-3): 1173-1185.
- Kawahara, F. K., B. Davila, S. R. Al-Abed, S. J. Vesper, J. C. Ireland, and S. Rock. 1995. Polynuclear aromatic hydrocarbon (PAH) release from soil during treatment with Fenton's reagent. *Chemosphere* 31(9): 4131-4142.

Kislenko, V. N., A. A. Berlin, and N. V. Litovchenko. 1997 Kinetics of oxidation of glucose by persulfate ions in the presence of Mn(II) ions. *Kinetics and Catalysis* 38(3): 391-396.

- Laperche, V., S. J. Traina, P. Gaddam, and T. J. Logan. 1996. Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite. *Environ. Sci. Technol.* 30: 3321-3326.
- Larson, S. L., C. L. Teeter, A. F. Medina, and W. A. Martin. 2007. *Treatment and management of closed or inactive small arms firing ranges*. ERDC/EL TR-07-6. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Li, Z. M., S. D. Comfort, and P. J. Shea. 1997a. Destruction of 2,4,6-trinitrotoluene by Fenton oxidation. *J. Environ. Qual.* 26: 480-487.
- Li, Z. M., P. J. Shea, and S. D. Comfort. 1997b. Fenton oxidation of 2,4,6-trinitrotoluene in contaminated soil slurries. *Environ. Eng. Sci.* 14(1): 55-66.
- Li, Z. M., P. J. Shea, and S. D. Comfort. 1998. Nitrotoluene destruction by UV-catalyzed Fenton oxidation. *Chemosphere* 36(8): 1849-1865.
- Liang, C., C. Bruell, M. Marley, and K. Sperry. 2003. Thermally activated persulfate oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries. *Soil Sed. Contam.* 12(2): 207-228.
- Liang, C., C. Bruell, M. Marley, and K. Sperry. 2004. Persulfate oxidation for in situ remediation of TCE: II. Activated by chelated ferrous ion. *Chemosphere* 55(9): 1225-1233.
- Lindsey, M. E., and M. A. Tarr. 2000. Inhibited hydroxyl radical degradation of aromatic hydrocarbons in the presence of dissolved fulvic acid. *Wat. Res.* 34(8): 2385-2389.
- Liou, M.-J., M.-J. Lu, and J.-N. Chen. 2003. Oxidation of explosives by Fenton and photo-Fenton processes. *Wat. Res.* 37: 3172-3179.
- Liou, M.-J., M.-C. Lu, and J.-N. Chen. 2004. Oxidation of TNT by photo-Fenton process. *Chemosphere* 57: 1107-1114.
- Lundstedt, S., Y. Persson, and L. Öberg. 2006. Transformation of PAHs during ethanol-Fenton treatment of an aged gasworks' soil. *Chemosphere*. 65(8): 1288-1294.
- Maenpaa, K. A., J. V. K. Kukkonen, and M. J. Lydy. 2002. Remediation of heavy metal-contaminated soils using phosphorous: Evaluation of bioavailability using an earthworm bioassay. *Arch. Environ. Contam. Toxicol.* 43: 389-398.
- Major, M. A., M. S. Johnson, and C. J. Salice. 2002. *Bioconcentration, bioaccumulation and biomagnification of nitroaromatic and nitramine explosives and their breakdown products.* Toxicology Study No. 87-4677-01, U.S. Army Environmental Center, Aberdeen Proving Ground, MD.
- Manchak, F. 1978. Methods of transforming sludge into ecologically acceptable solid material. U.S. Patent No. 4,079,003.

Marley, M. C., B. L. Cliff, K. L. Sperry, and J. M. Parikh. 2003. An evaluation of in situ chemical oxidation (ISCO) for MGP impacted soils and ground water. *Proceedings of the 19th Annual International Conference on Contaminated Soils, Sediments and Water.* University of Massachusetts at Amherst, Amherst, MA, October 20-23, 2003, CD-ROM.

- Maturi, K., and K. R. Reddy. 2006. Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin. *Chemosphere* 63: 1022-1031.
- McGrath, C. J. 1995. *Review of formulations for processes affecting the subsurface transport of explosives.* IRRP-95-2. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- McLaughlin, D., D. E. Armstrong, and A. W. Andren. 1993. Oxidation of polychlorinated biphenyl congener sorbed to particles. *Proceedings of the 48th Industrial Waste Conference*, p. 349-353. Boca Raton, FL: Lewis Publishers.
- Nadim, F., K.-C. Huang, and A. M. Dahmani. 2006. Remediation of soil and groundwater contaminated with PAH using heat and Fe(II)-EDTA catalyzed persulfate oxidation. *Water, Air, & Soil Pollution: Focus* 6(1-2): 227-232.
- Nam, K., W. Rodriquez, and J. J. Kukor. 2001. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction. *Chemosphere* 45(1): 11-20.
- National Research Council (NRC). 1999. Review and evaluation of alternative technologies for demilitarization of assembled chemical weapons. Appendix E. Neutralization of energetic materials by hydrolysis.

 www.nap.edu/openbook/0309066395
- Neyens, E., and J. Baeyens. 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mats.* B98: 33-50.
- Nisbet, C., and P. LaGoy. 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Reg. Toxicol. Pharmacol.* 16: 290-300.
- Oh, S.-Y., D. K. Cha, P. C. Chiu, and B. J. Kim. 2003a. Enhancing oxidation of TNT and RDX in wastewater: pre-treatment with elemental iron. *Wat. Sci. Technol.* 47(10): 93-99.
- Payne, J., F. Boelsing, A. Habekost, G. Hirschfeld, and V. Birke. 1991. *Complete ambient-temperature dehalogenation of PCBs in contaminated soil using hydrophobic lime and other reagents.* EPRI PCB seminar, Oct. 8-11, Baltimore, MD.
- Peyton, G. R., M. H. LaFaivre, and M. A. Smith. 1990. *Treatability of contaminated groundwater and aquifer solids at town gas sites using photocatalytic oxidation and chemical in situ oxidation*. Prepared for Illinois State Water Survey Division Report Rep. No. HWRIC-RR-048.
- Pitot, H. C., III, and Y. P. Dragan. 1996. Chemical carcinogenesis. In *Casarett and Doull's toxicology*, C. D. Klaassen, ed., *The basic science of poisons*, 5th ed. New York: McGraw-Hill, 201-267.

Premier Chemicals, LLC. 2005. EnviroBlend® heavy metal waste treatment products. http://www.enviroblend.com/

- Rodgers, J. D., and N. J. Bunce. 2001. Treatment methods for the remediation of nitroaromatic explosives. *Wat. Res.* 35(9): 2101-2111.
- Saupe, A., H. J. Garvens, and L. Heinze. 1998. Alkaline hydrolysis of TNT and TNT in soil followed by thermal treatment of the hydrolysates. *Chemosphere* 36(8): 1725-1744.
- Sedlak, D. L., and A. W. Andren. 1991. Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. *Environ. Sci. Technol.* 25(8): 1419-1427.
- Sedlak, D. L., K. E. Dean, D. E. Armstrong, and A. W. Andren. 1991. Interaction of quicklime with polychlorobiphenyl-contaminated solids. *Environ. Sci. Technol.* 25(11): 1936-1940.
- Sedlak, D. L., and A. W. Andren. 1994. The effect of sorption on the oxidation of polychlorinated biphenyls (PCBs) by hydroxyl radical. *Wat. Res.* 28(5): 1207-1215.
- Seok, J., J. Soek, and K.-Y. Hwang. 2005. Thermo-chemical destruction of polychlorinated biphenyls (PCBs) in waste insulating oil. *J. Hazard. Mats.* B124: 133-138.
- Soundararajan, R. 1991. *Appendix A. Final report on the "disappearing PCBs" project.* Fate of polychlorinated biphenyls (PCBs) in soil following stabilization with quicklime. EPA/600/2-91/052. Washington, DC.
- Sullivan, P. D., L. E. Ellis, L. M. Calle, and I. J. Ocasio. 1982. Chemical and enzymatic oxidation of alkylated benzo(a)pyrenes. *Chem. Biolog. Interact.* 40(2): 177-191.
- Tardy, B. A., R. M. Bricka, and S. L. Larson. 2003. *Chemical stabilization of lead in small arms firing range soils*. ERDC/ELTR-03-20. Environmental Quality and Technology Program. Vicksburg, MS: U.S. Army Engineer Research and Development Center.
- Thorne, P. G., T. F. Jenkins, and M. K. Brown. 2004. *Continuous treatment of low levels of TNT and RDX in range soils using surface liming.* ERDC/CRREL TR-04-4. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.
- Traina, S. J., and V. Laperche. 1999. Contaminant bioavailability in soils, sediments, and aquatic environments. *Proc. Natl. Acad. Sci.* 96: 3365-3371.
- Thyagarajan, B. S. 1983. Process for treatment of fluids contaminated with polychlorinated biphenyls. U.S. Patent number 4,612,404.
- United States Environmental Protection Agency (USEPA). 1994. *Method 200.7. Metals and trace elements by ICP/atomic emission spectrometry*. EPA/600/R-94/111.
- United States Environmental Protection Agency (USEPA). 1995. *Bench-scale testing of photolysis, chemical oxidation, and biodegradation of PCB contaminated soils, and photolysis of TCDD contaminated soils.* EPA/540/SR-94/531.

United States Environmental Protection Agency (USEPA). 2001. *Best management practices for lead at outdoor shooting ranges*. Technical Report EPA-902-B-01-001. U.S. Environmental Protection Agency, Region 2, New York, NY. www.epa.gov/region02/waste/leadshot/epa_bmp.pdf.

- United States Environmental Protection Agency (USEPA). 2004. *Drinking water standards and health advisories*. EPA/822/R-004-005.
- United States Environmental Protection Agency Integrated Risk Information System (USEPA-IRIS). 1997. 2,4,6-Trinitrotoluene (TNT). http://www.epa.gov/iris/subst/0269.htm
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1992. *Method 1311. Toxicity characteristic leaching procedure*. Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1994. *Method 3051. Microwave assisted acid digestion of sediments, sludges, soils, and oils.* Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1994. *Method 8330. Nitroaromatics and nitramines by high performance liquid chromatography (HPLC)*. Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1996. *Method 3545. Pressurized fluid extraction (PFE)*," Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1996. *Method 3630C. Silica gel cleanup.* Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1996. *Method 3665A. Sulfuric acid/permanganate cleanup.* Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1996. *Method 8082. Polychlorinated biphenyls (PCBs) by gas chromatography.* Washington, DC.
- United States Environmental Protection Agency, Office of Solid Waste Management, Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods (USEPA SW 846). 1996. *Method 8270C. Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)*. Washington, DC.
- Waisner, S. A., and G. E. Hoag. 2006. Fe(III)-EDTA persulfate destruction of explosives and pH dependence of chemistry. B. M. Sass, ed., Columbus, OH: Battelle Press, D-74. *Proceedings of the Fifth International Conference on Chlorinated and Recalcitrant Compounds*.

Wang, J.-Y., X.-J. Huang, J. C. M. Kao, and O. Stabnikova. 2006. Simultaneous removal of organic contaminants and heavy metals from kaolin using an upward electrokinetic soil remediation process. *J. Hazard. Mats.* 144(1-2): 292-299.

- Wang, Y. M., T. C. Chen, K. J. Yeh, and M. F. Shu. 2001. Stabilization of an elevated heavy metal contaminated site. *J. Hazard. Mats.* 88: 63-74.
- Watts, R. J., P. C. Stanton, J. Howsawkeng, and A. L. Teel. 2002. Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. *Wat. Res.* 36(17): 4283-4292.
- Weber, R., T. Takasuga, K. Nagai, H. Shiraishi, T. Sakurai, T. Matuda, and M. Hiraoka. 2002. Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration. *Chemosphere* 46: 1255-1262.
- Yoon, J., X. Cao, Q. Zhou, and L. Q. Ma. 2006. Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *Sci. Total Environ*. 368: 456-464.
- Yang, J., D. E. Mosby, S. W. Casteel, and R. W. Banchar. 2001. Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. *Environ. Sci. Technol.* 35: 3553-3559.

Appendix A: Draft Engineering Evaluation/Cost Analysis Report for Reservoir No. 2 Burning Ground, PBOW

IABL	E OF CONTENTS	
Sectio	on	Page
Execu	tive Summary	
1.0	INTRODUCTION	62
2.1	SITE DESCRIPTION AND BACKGROUND	68
2.1.1	Facility Location and History	68
2.1.2	2BG Site Description	
2.1.3	Surrounding Land Use, Populations, and Ecosystems	69
2.2	Previous Removal Actions	
2.3	SOURCE, NATURE, AND EXTENT OF CONTAMINATION	69
2.4	Remedial Objectives	
3.0	REMOVAL ACTION SCOPE, GOALS, AND OBJECTIVES	71
3.1	Justification for performance of a removal action	71
3.2	removal action scope and objectives	71
3.3	statutory limits on removal action	72
3.4	compliance with APPLICABLE OR RELEVANT AND	
	APPROPRIATE REQUIREMENTS	72
3.4.1	Overview	72
3.4.2	Method and Organization of the ARARs Analysis	····· 73
4.0	development of removal action alternatives	
4.1	technology identification and screening	····· 74
4.1.1	Technology Screening Summary	····· 74
4.1.2	Hydrated Lime Treatment	75
4.1.3	Lead Stabilization	76
4.1.4	In Situ Soil Tilling	76
4.1.5	Excavation	77
4.1.6	Windrow Composting	
4.1.7	Beneficial Reuse/On-Site Disposal	78
4.2	development of alternatives	
4.2.1	Alternative 1: No Action	
4.2.2	Alternative 2: Excavation, Stabilization, and Off-Site Disposa	l80
4.2.3	Alternative 3: Ex-situ Treatment	
4.2.4	Alternative 4: In Situ Treatment	
4.2.5	Alternative 5: Composting	83
5.0	ANALYSIS OF REMOVAL ACTION	
5.1	Evaluation Criteria	
5.1.1	Effectiveness	
5.1.2	Implementability	
5.1.3	Cost	86

5.2	Alternative 1: NO ACTION	87
5.2.1	Overall Protection of Public Health and Environment	8 [′] 7
5.2.2	Compliance with ARARs	
5.2.3	Long-Term Effectiveness and Permanence	87
5.2.4	Reduction of Toxicity, Mobility, or Volume through	ŕ
	Treatment	87
5.2.5	Short-Term Effectiveness	
5.2.6	Technical Feasibility	,
5.2.7	Administrative Feasibility	
5.2.8	Availability of Services and Materials	
5.2.9	State Acceptance	
5.2.10	Community Acceptance	88
5.2.11		
5.3	Alternative 2: EXCAVATION, Stabilization, AND off-site	
	disposal	88
5.3.1	Overall Protection of Public Health and Environment	88
5.3.2	Compliance with ARARs	89
5.3.3	Long-Term Effectiveness and Permanence	89
5.3.4	Reduction of Toxicity, Mobility, or Volume through	
	Treatment	_
5.3.5	Short-Term Effectiveness	
5.3.6	Technical Feasibility	
5.3. 7	Administrative Feasibility	
5.3.8	Availability of Services and Materials	
5.3.9	State Acceptance	
5.3.10	Community Acceptance	90
5.3.11		
5.4	Alternative 3: ex-situ treatment	
5.4.1	Overall Protection of Public Health and Environment	
5.4.2	Compliance with ARARs	
5.4.3	Long-Term Effectiveness and Permanence	92
5.4.4	Reduction of Toxicity, Mobility, or Volume through	
	Treatment	
5.4.5	Short-Term Effectiveness	
	Technical Feasibility	
5.4.7	Administrative Feasibility	93
	Availability of Services and Materials	
5.4.9	State Acceptance	
	Community Acceptance	
5.4.11		
5.5	Alternative 4: in situ treatment	94
5.5.1	Overall Protection of Public Health and Environment	
5.5.2	Compliance with ARARs	94
5.5.3	Long-Term Effectiveness and Permanence	94
5.5.4	Reduction of Toxicity, Mobility, or Volume through	^-
	Treatment	···· 95
5.5.5	Short-Term Effectiveness	95

5.5.6	Technical Feasibility	95
5.5.7	Administrative Feasibility	96
5.5.8	Availability of Services and Materials	
5.5.9	State Acceptance	
5.5.10	Community Acceptance	96
5.5.11		
5.6	Alternative 5: Composting	96
5.6.1	Overall Protection of Public Health and Environment	96
5.6.2	Compliance with ARARs	97
5.6.3	Long-Term Effectiveness and Permanence	
5.6.4	Reduction of Toxicity, Mobility, or Volume through	,
•	Treatment	97
5.6.5	Short-Term Effectiveness	
5.6.6	Technical Feasibility	
5.6.7	Administrative Feasibility	
5.6.8	Availability of Services and Materials	
5.6.9	State Acceptance	
	Community Acceptance	
5.6.11		
6.0	comparative analysis of removal action alternatives	
6.1	Overall Protection of Public Health and Environment	
6.2	Compliance With ARARs	
6.3	Long-Term Effectiveness and Permanence	
6.4	Reduction of Toxicity, Mobility, or Volume Through	,,
0.7	Treatment	aa
6.5	Short-Term Effectiveness	
6.6	TECHNICAL FEASIBILITY	
6.7	Administrative Feasibility	
6.8	Availability of Services and Materials	
6.9	State Acceptance	
6.10	Community Acceptance	
6.11	Cost	
7.0	recommended removal action alternative1	
7.1	COST	_
7.2	reduction of toxicity, mobility, or volume through treatment 1	
7. 2 7.3	Selection of The Preferred Alternative	
7.4	determination of removal schedule	
/ • -1	determination of removal beneaute	~ 4
Refere	ncesI	R-1

EXECUTIVE SUMMARY

This Engineering Evaluation/Cost Analysis (EE/CA) Report for Reservoir No. 2 Burning Ground (2BG) at Former Plum Brook Ordnance Works (PBOW) was prepared for the U.S Army Corps of Engineers (USACE) by Jacobs Engineering Group Inc (Jacobs).

PBOW was operated from 1941 to 1945 as a manufacturing plant for trinitrotoluene (TNT), dinitrotoluene (DNT), and pentolite. The 2BG site was used as a burning ground for process wastes during decommission of the facility. High levels of explosives were detected in the burn layer during the 2004 –2005 Remedial Investigation (RI).

The objective of this EE/CA Report is to provide an engineering evaluation and cost analysis of potential removal actions for soil remediation at 2BG, and to select a recommended removal action alternative based on effectiveness, implementability, and cost. The EE/CA process provides a screening and evaluation tool to identify appropriate removal action alternatives, furnishing sufficient information concerning the potential removal actions so that an informed decision can be made in selecting the most appropriate alternative. The removal action alternative that best satisfies the evaluation criteria based on a comparative analysis is identified in Section 7.0. The final selection of the removal action would be documented in an Action Memorandum.

Justification for performing this EE/CA is based upon detection of PCBs, explosives, PAHs, and lead exceeding the U.S. Environmental Protection Agency (USEPA) Region 9 preliminary remediation goals (PRGs) in site soil. Based on analytical sampling results in comparison with PRGs, contaminants in the surface and subsurface soils at 2BG represent a potential risk to human health and the environment. Potential routes of exposure include direct contact with soil as well as potential migration of contaminants to nearby surface water resources. Therefore, a removal action is justified to respond to the soil contamination.

Analytical data were screened against the PRGs to determine the extent and volume of contaminated soil. Approximately 3650 cubic yards of soil would require remediation.

The following alternatives were identified for evaluation:

- Alternative 1: No Action
- Alternative 2: Excavation, Stabilization, and Off-site Disposal
- Alternative 3: Ex-situ Lime Treatment
- Alternative 4: In-situ Lime Treatment
- Alternative 5: Composting

These five alternatives were evaluated, using several criteria that measure effectiveness, implementability, and cost.

Alternative 4 is the preferred alternative for remediating contaminated soil at the 2BG site. Alternative 4 offers the lowest cost because of the minimal amount of engineering required. Lime treatment is a proven method for reducing concentrations of PCBs, PAHs, DNT, and TNT as demonstrated through batch experiments in a laboratory setting using 2BG soil. The insitu approach would employ tilling of lime directly into the soil thus minimizing excavation and handling. To offset the uncertainties associated with tilling, multiple applications of lime would be used to maximize contact with the soil. Frequent testing of the soil pH would be conducted to confirm adequate alkaline hydrolysis reactions are occurring and to make adjustments as needed.

Alternative 2 was eliminated due to a greater percentage of waste requiring disposal at a RCRA facility outside of Erie County and due to the higher cost. Alternative 3 was eliminated because of cost, which was driven by excessive engineering measures. Alternative 5 was eliminated because of cost and uncertainty regarding treatment effectiveness due to high concentrations of 2,4 DNT and the coarse nature of the burn layer material.

Selecting Alternative 4 would result in the removal of approximately 1831 cubic yards (CY) of soil from the site while treating approximately 1822 CY for reuse on-site. Total cost for Alternative 4 would be approximately \$1,106,000. Alternatives 2, 3, and 5 would cost \$1,286,000, \$1,509,000, and \$1,360,000 respectively.

1.0 INTRODUCTION

This Engineering Evaluation/Cost Analysis (EE/CA) for contaminated soil at Reservoir No. 2 Burning Ground (2BG) at the former Plum Brook Ordnance Works (PBOW) in Sandusky, Ohio is being managed by the Corps of Engineers, Huntington District (CELRH) and technically overseen by the Corps of Engineers, Nashville District (CELRN). Jacobs Engineering Group Inc. (Jacobs) is conducting this work under contract DACW62-03-D-0004, Delivery Order #6.

The purposes of this EE/CA are to:

Identify and evaluate options for addressing contaminated soil at 2BG Satisfy environmental review requirements for remedial alternatives Provide a framework for evaluating remedial alternatives Support the selection of a preferred alternative Provide all information necessary for approval of an Action Memorandum

Section 104 of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) authorizes removal actions. The National Contingency Plan (NCP) at 40 Code of Federal Regulations (CFR) 300.415 describes the criteria necessary to implement a removal action of a hazardous substance at a CERCLA-regulated site. Specifically, the lead agency "may take any appropriate removal action to abate, prevent, minimize, stabilize, mitigate, or eliminate the release or the threat of release of hazardous substances." The lead agency must consider factors such as potential exposure or risk to human or ecological populations, drinking water, sensitive ecosystems, or the threat of additional releases, fires, explosions, or migration.

A removal action is warranted once the lead agency has determined that a threat exists, and may include emergency removal actions, time-critical removal actions (TCRAs), and non-time-critical removal actions (NTCRAs). Emergency removal actions and TCRAs should be conducted within six months of determining that a threat exists; NTCRAs may take longer. NTCRAs range in scope from small to substantial, multi-media response actions. An EE/CA must be performed once a decision is made to conduct a NTCRA. The EE/CA is similar in scope to a focused feasibility study (FS), containing only those data necessary to make a decision regarding the most appropriate removal alternative.

The remainder of this EE/CA Report is organized as follows:

Section 2.0 - <u>Site Characterization</u>, presents the history of the facility, site description, current land use, previous actions, and the nature and extent of contamination.

Section 3.0 - *Removal Action Scope, Goals, and Objectives*, presents justification for the action, action objectives and goals, and applicable or relevant and appropriate requirements (ARARs).

Section 4.0 - <u>Development of Removal Action Alternatives</u>, presents the technology screening, technologies evaluated, and a description of each alternative selected for further evaluation.

Section 5.0 – <u>Analysis of Removal Action</u>, presents the criteria used to evaluate alternative effectiveness, implementability, and cost, and measures each alternative by these criteria.

Section 6.0 – <u>Comparative Analysis of Removal Action Alternatives</u>, evaluates each alternative against each other in relation to the criteria used in Section 5.0.

Section 7.0 – *Recommended Removal Action Alternative*, presents the rational for the selected alternative.

Appendix A – <u>Contaminant Delineation Summary Report</u>, presents the results of the December 2005 sampling effort and the revised spatial distribution of contaminants.

Appendix B – *Waste Soil Volume Calculations*, provides the data and screening tools used to determine waste types and associated volumes.

Appendix C – <u>Supporting Cost Data</u>, provides detailed back-up cost information for each alternative.

Appendix D – <u>Treatability Study</u>, provides a summary of the treatment tests performed on 2BG soil and summarizes the results.

This EE/CA has been prepared in accordance with *Guidance on Conducting Non-Time Critical Removal Actions Under CERCLA* (USEPA 1993), and provides the information necessary for the preparation of an Action Memorandum by the Air Force.

2.0 SITE CHARACTERIZATION

2.1 SITE DESCRIPTION AND BACKGROUND

The following sections provide abbreviated descriptions of the Plum Brook facility and the 2BG site. More complete descriptions can be found in the Final Site Characterization Report (Jacobs 2006).

2.1.1 Facility Location and History

PBOW was operated from 1941 to 1945 as a manufacturing plant for trinitrotoluene (TNT), dinitrotoluene (DNT), and pentolite. The site is currently owned by the National Aeronautics and Space Administration (NASA) and is operated as the Plum Brook Station (PBS) of the John Glenn Research Center, located at Lewis Field, Cleveland, Ohio. NASA acquired PBOW in 1963 and presently utilizes about 6,400 acres for conducting space research. PBOW is located south of Sandusky, Ohio (Figure 2-1).

2.1.2 2BG Site Description

The 2BG site is located in the northwestern portion of PBOW approximately 400 ft south of Reservoir No. 2 at the former Plum Brook Station ball field between Ransom Road and Campbell Street (Figure 2-2).

The 2BG site was used as a burning ground for production process wastes. It is not known when the site was first used for burning; however, the 1950 aerial photo clearly shows the site to be in existence and photographs dated as late as 1962 show ongoing operations. Restoration of the site was

performed in 1963 when the area was cleared of debris and the ground restored to proper grade.

The 2BG site was used temporarily as a baseball field by NASA and is currently a grass-covered open field with young hardwood trees and surrounding brush.

The 2BG site physical features include a former burning ground located in an open field and a drainage ditch at the northern edge of the field. A paved service road is adjacent to the east side of the site. The ground surface is relatively flat, with minimal slope toward the north and northwest. Elevations at the site range from 639 to 641 feet above mean sea level (ft amsl). The majority of the site is currently an open field; however, the southern portion of the site and areas to the west are now wooded.

2.1.3 Surrounding Land Use, Populations, and Ecosystems

2BG is surrounded on all sides by NASA controlled property, which is fenced and maintained by security on a 24-hour basis. The area surrounding the site is wooded and is not being utilized by NASA. A few adjacent clearings north and west of the site are used on a periodic basis as wildlife research plots by the U.S. Department of Agriculture.

Current on-site human populations include occasional workers or visitors. There are no facilities being operated by NASA within 2000 feet of 2BG. The site is intended to be sold and made available to the public for unrestricted use.

2.2 PREVIOUS REMOVAL ACTIONS

Burning activities ceased in 1962 and in 1963 limited remediation of the site was performed, which included clearing of debris and restoring the ground to proper grade.

2.3 SOURCE, NATURE, AND EXTENT OF CONTAMINATION

An in-depth presentation of the source, nature, and extent of contamination is provided in the Final Site Characterization Report (Jacobs 2006) and in Appendix A, Contaminant Delineation Summary Report. This subsection summarizes the results relevant to the evaluation of remedial alternatives.

Contamination at 2BG was detected during surface and subsurface soil investigations performed as part of the Site Investigation in 1996, as part of the Remedial Investigation in 2004 and 2005, and during the EE/CA delineation sampling in December 2005.

Soil contamination at 2BG is concentrated within the footprint of the former burn area located west of the Reservoir No. 2 service road layer in the southeast corner of the clearing. The burn layer is approximately one foot below ground surface and averages one foot in thickness. Contamination within the burn area is confined primarily to the burn layer material and to a lesser extent in the surface soil above the burn layer. Contamination is also present in surface soil west of the burn area.

Contaminants exceeding the USEPA Region 9 Residential Preliminary Remediation Goals (PRGs), include explosives, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), dioxins, and lead.

Concentrations of 2,4 DNT and 2,4,6 TNT are greatest within the burn layer material, ranging from less than 1 percent to 4.5 percent by volume. Explosives concentrations are considerably lower in the surface soil above the burn layer. A few isolated areas of contamination are also present in the surface soil west of the burn area (Appendix A, Figure 4).

Concentrations of lead are greatest within the burn layer material. Elevated concentrations of lead are also present in the surface soil above the burn layer and in a few isolated areas in the surface soil west of the burn area (Appendix A, Figure 3).

Concentrations of PCBs are greatest in the surface soil above the burn layer. PCBs are most prevalent in the surface soil covering a large area northwest, west, and southwest of the burn area (Appendix A, Figure 2). PCBs are present in the burn layer material, but at significantly lower levels.

Concentrations of PAH compound bezo(a)pyrene are greatest in the surface soil west of the burn area (Appendix A, Figure 5). There were only two locations within the footprint of the burn area that exceeded the PRGs; one in the burn layer and one in the surface soil.

Multiple dioxin/furan compounds were detected in the soil and burn layer material; however, only one sample exceeded the PRGs. Dioxin/furan concentrations exceeded the land disposal restrictions (LDR) universal treatment standards (UTS) in 40 CFR 261 at one location.

2.4 Remedial Objectives

Human health and ecological risk assessments were not performed for the site; therefore site-specific risk-based remedial objectives were not calculated. USEPA Region 9 Residential PRGs (October 2004) have been used to delineate areas requiring remedial action and to calculate associated soil volumes for cost comparison purposes. Other remedial

objectives may be considered and proposed based on team discussions, which would be included in the future Action Memorandum.

3.0 REMOVAL ACTION SCOPE, GOALS, AND OBJECTIVES

3.1 Justification for performance of a removal action

The eight factors to be considered when determining the appropriateness of a removal action, as listed in 40 CFR 300.415 of the NCP, are as follows:

Actual or potential exposure to nearby human populations, animals, or the food chain from hazardous substances or pollutants or contaminants Actual or potential contamination of drinking water supplies or sensitive ecosystems

Hazardous substances or pollutants or contaminants in drums, barrels, tanks, or other bulk storage containers that may pose a threat of release High levels of hazardous substances or pollutants or contaminants in soil largely at or near the surface that may migrate

Weather conditions that may cause hazardous substances or pollutants or contaminants to migrate or to be released

Threat of fire or explosion

The availability of other appropriate federal or state response mechanisms to respond to the release

Other situations or factors that may pose threats to public health or welfare or the environment

Based on analytical sampling results compared to the USEPA Region 9 Residential PRGs, contaminants in the surface and subsurface soils at 2BG represent a potential risk to human health and the environment. Potential routes of exposure include direct contact with soil as well as potential migration of contaminants to nearby surface water resources. Therefore, a removal action is justified to address soil contamination.

3.2 removal action scope and objectives

The purpose of a removal action under Section 104 of CERCLA is to abate, minimize, stabilize, mitigate, or eliminate the release or threat of release of hazardous substances, pollutants, contaminants, or hazardous constituents. The primary objective of the removal action is to allow unrestricted use of the 2BG site. This objective would be met by remediation of contaminated soil that currently exceeds the USEPA Region 9 Residential PRGs for PCBs, explosives, PAHs, and lead.

The purpose of this EE/CA is to identify and evaluate options for remediating contaminated soil at 2BG and to recommend the alternative that best satisfies the evaluation criteria. The EE/CA considers those alternatives that could reasonably be expected to satisfy the objective of

the removal action. These alternatives are evaluated against the shortand long-term aspects of three broad criteria: effectiveness, implementability, and cost.

3.3 statutory limits on removal action

Pursuant to Section 104(c)(1) of CERCLA, fund-financed removal actions (other than those authorized under Section 104[b] of CERCLA) shall be terminated after \$2 million dollars have been obligated for the action or 12 months have elapsed from the date that removal activities begin on site (40 CFR 300.415[b][5]). This is the case unless the lead agency determines that there is an immediate risk to public health or welfare or the environment, or continued response action is otherwise appropriate and consistent with the remedial action to be taken.

While much of 40 CFR Part 300, subpart E (where 40 CFR 300.415[b][5] is found) is oriented toward federally funded response actions, subpart E may be used as guidance concerning methods and criteria for response actions by parties under other funding mechanisms (40 CFR 300.400[I][2]).

Because the NTCRA at 2BG is not a fund-financed removal action, the \$2 million dollar funding ceiling and 12-month completion period limit are not applicable. Additionally, although CERCLA Section 120(a) requires federal facilities to comply with CERCLA to the same extent as any nongovernmental entity, CERCLA Section 120(a)(3) states that this requirement does not apply with respect to schedule.

3.4 compliance with APPLICABLE OR RELEVANT AND APPROPRIATE REQUIREMENTS

3.4.1 Overview

The NCP at 40 CFR 300.415(i) requires that on-site removal actions selected under Section 104 of CERCLA must, to the extent practicable considering the exigencies of the situation, attain (or have waived) any federal environmental or more stringent state environmental or facility siting standards, requirements, criteria, or limitations that are determined to be legally applicable or relevant and appropriate to conditions, contaminants, and/or actions at the site. The following is a general discussion of requirements for the identification of ARARs.

ARARs generally are divided into location-, chemical-, and action-specific requirements. Location-specific ARARs restrict actions or contaminant concentrations in certain environmentally sensitive areas. Chemical-specific ARARs are usually promulgated health- or risk-based numerical values or methods used to determine acceptable concentrations of

chemicals that may be found in, or discharged to, the environment. Action-specific ARARs are usually technology- or activity-based requirements or limitations on actions taken with respect to hazardous wastes.

An on-site action need only comply with substantive parts (and not administrative parts) of requirements identified as ARARs. The NCP at 40 CFR 300.400(e)(1) also exempts on-site actions from having to obtain federal, state, or local permits. However, on-site actions must still be in compliance with any substantive permit requirements. Off-site actions must comply only with requirements that are legally applicable, but they must comply with both the substantive and the administrative parts of those requirements. Permits, if required, must be obtained for any removal activities conducted off site (40 CFR 300.400[e][2] of the NCP). Statutory waivers may not be used for off-site actions. In addition to ARARs, the NCP at 40 CFR 300.400(g)(3) states that federal or state non-promulgated advisories or guidance "may, as appropriate," be identified to-be-considered (TBC) for contaminants, conditions, and/or actions at the site. TBCs are not ARARs because they are neither promulgated nor enforceable. TBCs may be used to interpret ARARS, or to determine preliminary remediation goals when ARARS do not exist for particular contaminants or where ARARs are not sufficiently protective to develop cleanup goals.

3.4.2 Method and Organization of the ARARs Analysis

Federal and State of Ohio regulations and guidance documents were reviewed to identify potential location-, chemical-, and action-specific ARARs and TBCs for the proposed alternatives in this EE/CA. Where the USEPA has delegated to the State of Ohio the authority to implement a federal program, regulations in the state's delegated program would replace the equivalent federal requirements as the potential ARARs. The final determination of ARARs rests with the regulatory agencies. The determination of the potential use of TBCs rests with the Plum Brook team.

A detailed analysis of federal and State of Ohio requirements was conducted to determine their potential applicability or relevance and appropriateness in relation to conditions, contaminants, and/or actions at 2BG. A list of the identified ARARs and TBCs for each proposed alternative is provided in Tables 3-1 and 3-2 (location- and action-specific ARARs, respectively) of this EE/CA Report. No chemical-specific ARARs were identified.

4.1 technology identification and screening

The primary objective of the removal action is to allow unrestricted use of the 2BG site. Technology screening and subsequent alternative development was performed to ensure this objective is met.

4.1.1 Technology Screening Summary

A technology screening was conducted to identify certain technologies that could meet the remedial objectives. Several categories of technology were considered, which included the following:

Institutional Controls
Excavation and Disposal
Ex-Situ Treatment
In-Situ Treatment

Based on this screening, several promising technologies were identified and evaluated as part of the 2BG treatability study. The treatability study involved the collection of bulk samples from the 2BG site, pre-treatment chemical analysis, batch reactor studies, and post-treatment chemical analysis to gauge the treatment effectiveness. Soil collected from the site included surface soil above the burn layer, burn layer material, and surface soil west of the burn area. Chemical analysis included nitroaromatics, PCBs, PAHs, and lead. The batch reactor studies included the following:

1.5% lime slurry 5,000 mg/L persulfate slurry 10,000 mg/L persulfate slurry Fenton's Reagent Phosphate – 3% Enviroblend Phosphate – 5% Enviroblend

Results from the treatability studies indicate that the lime slurry was the most effective at reducing the concentration of TNT, DNT, PCBs, and PAHs. The studies also confirmed the effectiveness of phosphate to stabilize the lead in the 2BG soil. The Treatability Study Summary Report is provided in Appendix D.

Technologies associated with institutional controls included fencing, capping, and land-use restrictions. All of these options were screened out because they do not meet the primary objective of unrestricted reuse.

Excavation and disposal options included off-site disposal, on-site disposal, and a combination of the two options. All of the excavation and disposal options were carried forward as these are very reliable technologies for addressing contaminated soil.

The ex-situ treatment technologies evaluated included hydrated lime, persulfate, phosphate, incineration, low-temperature thermal desorption (LTTD), and composting. Incineration was screened out due to high treatment cost and the presence of PCBs, that break down into dioxins/furans when burned. Likewise, the LTTD option was screen-out because it is not effective at treating PCBs. Persulfate was evaluated and tested as part of the 2BG treatability study, but was screened out because the lime treatment was more effective at reducing the concentrations of TNT and DNT. Lime, phosphate, and composting were retained for further evaluation.

The in-situ treatment technologies evaluated included tilling with lime, bioremediation injection, electrochemical GeoOxidation, grouting, chemical stabilization, and phytoremediation (plants). The grouting and chemical stabilization alternatives were screened out because they do not meet the unrestricted reuse objective. The bioremediation, electrochemical, and phytoremediation options were screened out because these technologies can not effectively treat all of the contaminants present in the 2BG soil. Tilling with lime was retained for further evaluation because of the favorable results during the 2BG treatability study.

The technologies considered in this EE/CA Report are as follows:

Hydrated lime treatment
Lead stabilization (phosphate)
In-situ soil tilling (lime)
Excavation
Off-site disposal
Composting
Beneficial reuse

4.1.2 Hydrated Lime Treatment

Lime treatment increases the pH of the system, making the explosives (TNT and DNT) amenable to decomposition by alkaline hydrolysis. This degradation was demonstrated through a treatability study performed by the U.S. Army Engineer Research and Development Center (ERDC) in support of this EE/CA. The treatability study (Appendix D) was performed using soil samples collected from the burn area and surface soils west of the burn area. Treatment efficiency depends upon adequate mixing, achieving the target pH of the slurry, and mixture residence time.

Lime treatment would be conducted by adding hydrated lime (CaH2O2) to a soil and water slurry to elevate the pH of the mixture to 11. The mixture would be allowed to react for a minimum of 24 hours. Based on the treatability study, it is expected that TNT in the soil would decrease by approximately 90 percent in 24 hours, levels of DNT and benzo(a)pyrene

would decrease by approximately 70 pecent and 40 percent, respectively, and levels of PCB would decrease by approximately percent.

4.1.3 Lead Stabilization

The treatability study also investigated phosphate treatment for stabilizing lead. Phosphate treatment of lead contaminated soil stabilizes the matrix by forming of insoluble minerals. The investigation focused on the addition of 3-5 percent of a commercially available phosphate mineral called Enviroblend. Previous studies have shown that this range is effective in stabilizing lead in most soil conditions. The treatability study concluded that this treatment decreased the TCLP extraction of lead in the soil by greater than 99 percent.

As phosphate treatment is a stabilization process and does not reduce the toxicity or volume of lead in the soil, this technology would only be applied to alternatives where treatment is combined with excavation and off-site disposal. Stabilization of lead prior to disposal would allow disposal of the treated soil at a more cost-effective disposal facility.

Depending on the activities required for each alternative, lead stabilization may be performed ex situ or in situ. Ex situ treatment would involve mixing the soil and phosphate mineral in a paddle mixer or other equivalent mixer. In situ treatment would be performed by tilling the phosphate mineral into the contaminated soil and then excavating the treated soil for subsequent packaging and disposal.

4.1.4 In Situ Soil Tilling

Soil tilling with amendments such as hydrated lime encourages in-situ decomposition by alkaline hydrolysis. Alkaline hydrolysis is a well established method for the destruction of explosives compounds. Previous studies have shown that hydrated lime effectively destroys explosives compounds soil. As described in section 4.1.1, elevating the pH of the soil to 11 with the addition of lime results in a significant reduction of TNT, DNT, PCBs, and benzo(a)pyrene.

Studies performed at ERDC show that a well-mixed hydrated lime treatment is significantly more effective than a topical application of lime. In order to reproduce this level of effectiveness at 2BG, several rounds of mixing and reaction might be required to ensure that adequate mixing, contact/reaction, and residence time are available for hydrolysis. Once the lime is mixed into the soil through tilling with a rotovator, water may be applied to the tilled soil to further dissolve the lime to elevate the pH of the soil and as a dust suppression measure during tilling.

4.1.5 Excavation

The extent of contamination at 2BG was defined during soil investigations as part of the remedial investigation (RI) conducted in 2004 and 2005 and during additional delineation sampling as part of the EE/CA in December 2005. Final contaminant delineation maps are provided in Appendix A. The investigation data, contaminant boundaries, and the reduction rates from the treatability study form the basis for the excavation volume estimates. Additional detail on the soil volume estimates including figures and analytical tables are provided in Appendix B.

Prior to excavation activities at the site, the extent of the PCB contamination zones, lead contamination zones, DNT hotspots, and the burn area would be marked on site with landscaping spray paint. This delineation would provide the initial basis for waste segregation, which would be confirmed both through laboratory analysis once the soil is excavated and packaged and through site confirmation sampling after removal action activities are complete.

Excavation to a depth of 12 inches or less would be performed using a bulldozer. Excavation to depths greater than 12 inches would be performed using a backhoe/loader. Soil removal at the burn area would progress to an average depth of 3 feet and to a lateral extent as delineated by spray paint on the ground surface as visually confirmed by site personnel.

Based on the RI, it is expected that untreated soil excavated from within the footprint of the burn area and from select surface hotspots west of the burn area would be considered Resource Conservation and Recovery Act (RCRA) hazardous waste. The amount of hazardous soil is estimated to be 1816 cubic yards (CY), which if untreated would require disposal at a RCRA Subtitle C waste disposal facility. The remaining contaminated soil west of the burn area would require excavation and disposal at the local sanitary disposal facility if left untreated. The amount of non-hazardous soil requiring remedial action is estimated at 1972 CY. Waste generated would be characterized to ensure conformance with the waste acceptance criteria (WAC) of the appropriate off-site disposal facility.

Excavation and off-site disposal is included in every remedial alternative discussed below as a result of lead concentrations above the PRGs. All of the soil within the footprint of the burn area and at select hotspots west of the burn area would require off-site disposal. The use of phosphate stabilization as a treatment alternative would allow disposal of this soil at the local sanitary landfill.

4.1.6 Windrow Composting

Ex-situ bioremediation through composting is a demonstrated technology for addressing a variety of organic contaminants, including nitroaromatic compounds. Windrow composting was recently used successfully to reduce nitroaromatic contaminant concentrations in soil from the TNT Area B and Pentolite Road Red Water Pond Area at Plum Brook Ordnance Works.

The length of time required for the composting process to achieve the desired contaminant reduction depends on several conditions that promote microbial activity including carbon-to-nitrogen ratio, moisture, aeration, and temperature. The carbon-to-nitrogen ratio of a material is an estimate of the relative amounts of these two elements in the material. A ratio of 30:1 to 20:1 is necessary to supply microbes with the carbon required to produce energy and perform protein syntheses. The recommended moisture level range for the compost is 50 percent to 70 percent. If the compost materials are too wet, the moisture results in compaction of the mix and restrict airflow, contributing to the formation of anaerobic conditions. Aeration provides microbes with the oxygen required to efficiently break down organic material. Aeration is achieved by routinely turning the compost and the use of bulking agents to increase the void space within the composting piles. Microbial activity increases the temperature of the compost, which allows for rapid decomposition. However, at temperatures above 160 °F, the compost can become sterile. The recommended temperature range for composting is between 90 to 140 °F.

To determine the appropriate "recipe" or optimum mixture of soil, moisture, bulking agents, temperature, and organic material such as chicken or cow manure, a bench scale study would be required. Excavated soil from 2BG contaminated with nitroaromatic constituents would be combined with amendments in accordance with the approved recipe with a windrow composter. Based on the bench scale study and field conditions, additional amendments and water might be required. Also, routine aeration with the windrow composter would be performed to maintain appropriate temperature and oxygen content in the composting rows.

4.1.7 Beneficial Reuse/On-Site Disposal

To the extent practicable, alternatives were developed to incorporate beneficial reuse of generated material. Beneficial reuse of material generated during a removal action reduces the overall volume of waste requiring disposal and may provide other financial incentives such as reducing the amount of backfill material required to restore the site.

Several areas of the site are currently covered with brush and trees. In order to excavate or treat the soil in these areas, the trees and brush must be removed. Brush (small shrubs and trees) would be cut near the ground surface. The trees would be cut near the surface and the stump and roots would be removed with excavation equipment. Trees, stumps/roots, and brush would be collected and reduced with a drum shredder. After shredding, this organic material could be stockpiled and subsequently used as compost during site restoration.

Treated soil that does not contain lead above risk levels may be reused as backfill material for the site during site restoration. Prior to use as backfill, the treated soil would be sampled to confirm that the soil does not pose unacceptable risk to human health or the environment.

4.2 development of alternatives

Based on the selected technologies described in Section 4.1, four removal action alternatives were developed that are considered capable of meeting the removal action goals for the site (unrestricted/residential use). In addition to these four alternatives, the option to leave the site in its current state (no action) is also evaluated. The alternatives being evaluated are as follows:

Alternative 1 – No Action

Alternative 2 – Excavation, Stabilization, and Off-Site Disposal

Alternative 3 – Ex-situ Treatment

Alternative 4 – In Situ Treatment.

Alternative 5 – Composting

Each of these alternatives is presented in detail in Sections 4.2.1 through 4.2.5.

4.2.1 Alternative 1: No Action

The no action alternative would involve leaving the property in its current state. The no action alternative provides a comparative baseline against which other alternatives are evaluated. Under this alternative, no removal action would be taken and contaminants would be left "as is," without the implementation of containment, removal, treatment, or other remedial actions. This alternative does not provide for the monitoring of environmental media such as soil at the site and does not provide any institutional controls such as fencing or deed restrictions to reduce the potential for human exposure.

4.2.2 Alternative 2: Excavation, Stabilization, and Off-Site Disposal

This alternative would involve excavation of the burn area and hazardous soil hot spots, stabilization of lead containing soil, excavation of remaining contaminated soil, waste characterization, and transportation to appropriate off-site disposal facilities. Contamination areas would be marked in the field based on the delineation study results (Appendix A). Excavation to a depth of 12 inches or less would be performed using a bulldozer, which would be used for removal of all contaminated surface soil. Excavation of the burn layer would be performed using a backhoe/loader. Soil removal at the burn area would progress to an average depth of 3 feet and to a lateral extent as delineated by spray paint and as visually confirmed by site personnel.

Stabilization treatment would involve combining the lead contaminated soil and a phosphate mineral such as Enviroblend with a rapid mixer.

Any soil characterized as RCRA hazardous would be transported to a RCRA subtitle C landfill for disposal. Soil characterized as RCRA non-hazardous would be transported to a sanitary landfill for disposal.

Soil would be excavated and segregated based on the contaminant delineation that has already been performed at the site, as well as confirmatory sampling to be performed as part of the removal action to ensure that soil exceeding the clean-up levels are removed. Excavation and segregation of soil types would be performed as shown in Figure 4-1. The segregation of soil types is based primarily on the disposal cost which is driven by the contaminant(s) of concern (COC) and the concentration levels. Quoted rates for disposal of material exceeding 3 percent explosives by volume is \$900/CY and material with dioxins/furans exceeding the LDR UTS are \$450/CY. Estimated soil volumes and the associated disposal costs for the various soil types considered for Alternative 2 are provided in Appendix B, Table B-1. Alternative 2 assumes that the volume of hazardous soil is 555 CY and the volume of non-hazardous soil is 3098 CY.

Soil would be segregated during excavation, packaged in accordance with state, federal, and local requirements, characterized to ensure that the waste meets the requirements for the disposal facility, and transported to the appropriate disposal facility.

Soil backfill material would be selected from either on-Base or off-Base sources. The cost estimate assumes an off-Base source would be used. The soil backfill material would be tested for COCs by collecting at least three samples from the source and submitting the samples to an analytical laboratory for analysis. Soil backfill and shredded organic material from

site clearing would be used to regrade the excavated site. Once the backfill material is placed and graded, the site would be re-seeded.

As part of this alternative, ambient air monitoring would be performed at the perimeter of the excavation area. The purpose of air monitoring is to protect the health of site workers, and to assess off-site migration of contaminants. The regulatory provisions governing erosion and sediment control, storm water management, fugitive dust emissions, noise control, and hazardous waste accumulation are identified in Section 3.4 as potential action-specific ARARs for this proposed removal action.

4.2.3 Alternative 3: Ex-situ Treatment

This alternative would involve excavation as described in Alternative 2, lime treatment to address TNT, DNT, benzo(a)pyrene, and PCB; stabilization of lead contamination with phosphate; characterization of treated waste; and transportation to an appropriate off-site disposal facility or reuse on site as backfill. If the post treated soil is characterized as RCRA non-hazardous, it would be transported to a sanitary landfill for disposal. Treated soil that meets the PRG concentration levels for DNT, TNT, PCBs, PAHs and lead would be used as on-site backfill material.

As described for Alternative 2, the site would be delineated such that soil is segregated during excavation. Excavated soil would be treated with hydrated lime. Soil would be placed in a large-scale mixer (i.e., concrete truck, cement mixer, etc.) and a 1 to 1 ratio of water would be introduced to the soil to produce a slurry. 1.5 percent hydrated lime would be added to the slurry to raise the pH to 11. The slurry would be thoroughly mixed for 30 to 60 minutes. After mixing, the slurry would be placed in a holding container (i.e., rolloff box, tank, etc.). The slurry would remain in the tank for a residence time of at least 24 hours.

After residence time is achieved for each tank, the water from the top of the settled soil would be removed with a submersible pump. The remaining slurry would be removed from the tank and dewatered using a filter press. The water recovered through pumping and dewatering may be reused for subsequent lime treatment batches. Treated soil that is not contaminated with lead would be characterized, loaded onto dump trucks, and transported to a local sanitary landfill. Lead contaminated soil would receive a second stage of treatment for lead stabilization.

Stabilization treatment would involve combining the contaminated soil and a phosphate mineral such as Enviroblend with a rapid mixer. The stabilized soil would be characterized, loaded onto dump trucks, and transported to a local sanitary landfill. If any of the treated and/or stabilized soils did not meet the WAC for the sanitary landfill, the soil would be placed into intermodal containers for transport to an off-site

hazardous waste landfill. Based on the existing data, it is likely that DNT contamination in the southern portion of the burn layer would not achieve the waste acceptance criteria for the local sanitary landfill after in-situ treatment. This treated soil would be placed into intermodal containers and transported to a RCRA treatment storage disposal facility (TSDF) for disposal.

Soil would be excavated and segregated based on the contaminant delineation that has already been performed at the site, as well as confirmatory sampling to be performed as part of the removal action to ensure that soil exceeding the PRGs are removed. Excavation and segregation of soil types would be performed as shown in Figure 4-2. Soil volumes and waste soil types are based on delineation sampling and concentration reduction factors determined during the treatability study. Estimated soil volumes and the associated disposal cost for the various soil types considered for Alternative 3 are provided in Appendix B, Table B-2.

Following is an example of how the concentration reduction factors have been applied to the existing sample results to determine waste type and waste volumes. Based on the treatability studies, lime hydrolysis is effective at reducing 2,4 DNT by 75 percent. Based on a toxicity characteristic leaching procedure (TCLP) analysis performed on posttreated, soil the total 2,4 DNT concentration vs. the extraction concentration showed a reduction of 850:1 (62mg/kg vs. 0.073 mg/L). The regulatory limit for 2,4 DNT (TCLP) is 0.13 mg/L. Concentrations of 2,4 DNT in the southern half of the burn layer range from 635 to 9700 mg/kg. These concentrations would result in a TCLP extraction value of 0.19 to 2.85 mg/L, well above the regulatory limit. Therefore, lime hydrolysis would not effectively treat 2,4 DNT in much of the burn layer material. By applying the lime hydrolysis reduction factor of 75 percent and the TCLP extraction factor of 850:1 to the regulatory limit of 0.13 mg/L, the maximum concentration for effective treatment can be determined as follows:

$$((0.13*850)/0.25 = 442 \text{ mg/kg})$$

Similar reduction calculations were applied to the sample data for 2,4,6 TNT, PCBs, benzo(a)pyrene, and lead, which are presented in Appendix B.

Site backfilling and restoration activities for this alternative would be as described for Alternative 2. The regulatory provisions governing erosion and sediment control, storm water management, fugitive dust emissions, noise control, and hazardous waste accumulation are identified in Section 3.4 as potential action-specific ARARs for this proposed removal action.

4.2.4 Alternative 4: In Situ Treatment

Alternative 4 incorporates all of the components performed in Alternative 3, but the lime treatment would be performed in-situ by using a tiller/rotovator to mix the lime into the soil. A layer of hydrated lime would be spread over the surface area to be treated. The lime would be mixed into the soil to approximately 12 inches. Several passes with a tractor-pulled rotary tiller would likely be required to ensure thorough mixing of the lime. The tilled area would be sprayed with water to encourage the lime to dissolve and would be left in place for approximately one week.

Samples would be collected of the tilled soil and field screened to evaluate the effectiveness of the treatment. Based on field screening results, additional rounds of treatment might be required to achieve the treatment objectives for TNT, DNT, benzo(a)pyrene, and PCB. The lime treated soil would be left on site and mixed with soil backfill and shredded organic material from site clearing. The area would be regraded and the site would be re-seeded.

Alternative 4 would also involve excavation and disposal of untreated burn layer material as well as excavation and ex-situ treatment for lead stabilization, with subsequent disposal at a local sanitary landfill. Soil would be excavated and segregated based on the contaminant delineation previously performed at the site as well as confirmatory sampling to be performed as part of the removal action to ensure that soil exceeding the PRGs are removed or treated. Excavation, segregation of soil types, as well as the in-situ treatment would be performed as shown in Figure 4-3. Soil volumes and waste soil types are the same as those for Alternative 3 (Appendix B, Table B-3).

4.2.5 Alternative 5: Composting

This alternative incorporates windrow composting for the treatment of 2,4 DNT in the burn layer material to eliminate the need for hazardous waste disposal at a RCRA landfill. All other excavation activities and in-situ lime treatment would be performed as proposed in Alternative 4.

During the design phase of this alternative, a bench-scale treatment study would be performed to test the effectiveness of a variety of composting recipes. Approximately five recipes would be tested to identify the most effective amount of organic matter, bulking agents, soil, temperature, and moisture for rapid compost treatment of 2BG soil. Concurrent with the bench study, additional field sampling (primarily field screening with 20 percent confirmatory laboratory analysis) would be conducted to collect additional nitroaromatic soil contamination data for the burn area. This

data would support soil segregation within the burn area such that only the highest concentrations of DNT are targeted for compost treatment.

After in-situ tilling and excavation of contaminated soil is complete, the site would be prepared for composting. The former burn area would be converted into a drainage area to catch residual runoff from the windrow composting. The drainage area would be lined with a high density polyethylene (HDPE) liner and would serve as a temporary retention pond. The area to the west of the burn area would be reconfigured to serve as the composting area. A 12-inch layer of gravel would be placed over the treatment area to provide a permeable layer under the compost row. An earthen berm would be installed around the perimeter to contain the treatment area. A trench would be installed to divert water from the treatment area to the drainage area.

Water collected in the drainage area from precipitation would be pumped into two 21,000 gallon frac tanks to prevent overflow. Water collected in the frac tanks may be used to spray the compost pile as needed to maintain optimum moisture.

Stockpiled soil for composting would be screened to remove materials larger than 1.5 inches in diameter prior to placement in the treatment area. Bulking agents and soil would be placed into a row approximately 20 ft wide and 100 ft long. Organic amendments would be added to the row in accordance with the approved recipe and the row would be sprayed with water to increase the moisture content. The row would be mixed to incorporate the soil, amendments, and bulking agents into a compost pile with a windrow composter.

It is likely that the composting process would require daily aeration through windrow composting, weekly spraying of water to maintain moisture, and periodic addition of straw and organic material into the compost pile to maintain microbial activity. The pile would be monitored daily for temperature and moisture. In addition, air monitoring for parameters such as ammonia, methane, and carbon monoxide would be required to ensure the safety of personnel. Field screening for nitroaromatics would be performed weekly to evaluate the degradation of contaminants in the compost pile.

The composting project performed on soil from TNT Area B required on average 4 to 6 weeks to reach the objective concentration levels. It is assumed that the 2BG composting process would require approximately 12 weeks, based on much higher concentrations of 2,4 DNT and the coarse texture of the burn layer material. This assumption would be re-evaluated based on the results of the bench-scale study.

Soil segregated for composting would also require treatment for lead contamination through phosphate mineral stabilization. After the composting process is completed, the treated soil and composting material would be loaded onto dump trucks and transported to a local sanitary landfill for disposal.

Excavation, segregation of soil types, as well as the in-situ treatment and composting would be performed as shown in Figure 4-4. Estimated soil volumes and the associated disposal cost for the various soil types considered for Alternative 5 are provided in Appendix B, Table B-4.

Site backfilling and restoration activities for this alternative would be as described for Alternative 2. The regulatory provisions governing erosion and sediment control, storm water management, fugitive dust emissions, noise control, and hazardous waste accumulation are identified in Section 3.4 as potential action-specific ARARs for this proposed removal action.

5.0 ANALYSIS OF REMOVAL ACTION

This section presents the evaluation of alternatives against the short- and long-term aspects of three broad criteria: effectiveness, implementability, and cost. Sub-criteria under each of these criteria are described in Section 5.1. These criteria are analogous to the nine criteria for a CERCLA FS (40 CFR 300.430[e][9][iii]).

5.1 Evaluation Criteria

The following sections outline the criteria for evaluation of removal action alternatives.

5.1.1 Effectiveness

The effectiveness of an alternative refers to its ability to meet the objectives of the removal action. The following sub-criteria are evaluated:

Overall Protection of Public Health and Environment. This sub-criterion encompasses evaluation of protectiveness of public health and the environment. The discussion focuses on how each alternative achieves adequate protection and draws on assessments conducted under other evaluation criteria, including long-term effectiveness and permanence, short-term effectiveness, and compliance with ARARs.

<u>Compliance With ARARs</u>. Section 300.415(I) of the NCP requires that removal actions under CERCLA attain ARARs to the extent practicable considering the exigencies of the situation and the scope of the removal. Evaluation under this sub-criterion summarizes which requirements are

applicable or relevant and appropriate to an alternative and describes how the alternative meets those requirements.

<u>Long-Term Effectiveness and Permanence</u>. This evaluation assesses the effectiveness of the removal action over the long term, including an evaluation of the ongoing operation and maintenance (O&M) required for each alternative.

Reduction of Toxicity, Mobility, or Volume through Treatment. This subcriterion addresses the USEPA's preference for treatment processes that would permanently and significantly reduce toxicity, mobility, or volume of the hazardous substances.

<u>Short-Term Effectiveness</u>. The short-term effectiveness sub-criterion addresses the effects of the alternative during implementation, including risks to the community that result from implementation, threats to site workers, potential adverse environmental impacts, and an estimate of the time needed to achieve the removal objective.

5.1.2 Implementability

The implementability criterion addresses the technical and administrative feasibility of implementing an alternative, and the availability of various materials and services required for implementation. The following subcriteria are evaluated:

<u>Technical Feasibility</u>. Evaluation under this sub-criterion examines technical difficulties, operational difficulties, and the general reliability associated with each alternative.

<u>Administrative Feasibility</u>. Administrative feasibility evaluates the activities requiring coordination with other offices and agencies, including the need for permits or waivers.

<u>Availability of Services and Materials</u>. This evaluation determines whether the personnel, equipment, and services necessary to implement an alternative are available in time to maintain the removal action schedule.

<u>State Acceptance</u>. This sub-criterion addresses technical or administrative concerns that the state may have.

<u>Community Acceptance</u>. This evaluation assesses potential concerns that the local community may have.

5.1.3 Cost

Each alternative is evaluated to determine its projected costs within a +50 to -30 percent range. The cost evaluation focuses on the direct and

indirect capital costs, since ongoing O&M costs are not expected. The following items are considered capital costs:

Direct capital costs: construction equipment and material transportation and disposal analytical contingency allowances

Indirect capital costs engineering and design expenses.

5.2 Alternative 1: NO ACTION

5.2.1 Overall Protection of Public Health and Environment

This alternative would not be protective of human health and environmental receptors because no action would be taken to reduce the concentrations of COCs in soil to meet Ohio Environmental Protection Agency (OEPA) risk management criteria or to prevent current or future receptors from exposure to the COCs.

5.2.2 Compliance with ARARs

Pursuant to EPA guidance (OSWER Directive 9234.2-01/FS-A, June, 1991), there are no ARARs for a no action alternative. The no action alternative, however, would not meet the threshold criterion of protection of human health and the environment.

5.2.3 Long-Term Effectiveness and Permanence

This alternative would not result in any permanent reduction of risk to human health of the environment. No periodic review would take place to evaluate future site conditions.

5.2.4 Reduction of Toxicity, Mobility, or Volume through Treatment

This alternative does not employ any remedial component that would permanently or significantly reduce the toxicity, mobility, or volume of contaminants in soil.

5.2.5 Short-Term Effectiveness

There are no short-term impacts from this alternative because no remedial action is taken.

5.2.6 Technical Feasibility

This alternative is technically feasible.

5.2.7 Administrative Feasibility

This alternative is not administratively feasible as it is likely that OEPA would require action to be taken to address soil contamination at 2BG.

5.2.8 Availability of Services and Materials

There are no issues related to the availability of services and materials for this alternative as no services or materials are required.

5.2.9 State Acceptance

It is highly unlikely that OEPA would accept the no-action alternative for soil contamination at 2BG because this alternative is not protective of human health.

5.2.10 Community Acceptance

It is highly unlikely that the community would accept the no-action alternative for soil contamination at 2BG because it does not address the soil contamination and is not protective of human health.

5.2.11 Cost

There is no cost impact associated with this alternative.

5.3 Alternative 2: EXCAVATION, Stabilization, AND off-site disposal

5.3.1 Overall Protection of Public Health and Environment

This alternative is expected to effectively reduce risks to human health and the environment by removing contaminated soil from 2BG, on-site stabilization of lead contaminated soil, and disposing of this soil at a permitted off-site disposal facility. Contaminants would be removed from the site by this alternative to allow unrestricted use of the site. Worker exposure to contaminants during implementation of this alternative would be controlled by following a site-specific health and safety plan (HSP). Adherence to the requirements of the HSP would prevent contact with and inhalation of contaminants through the use of administrative and engineering controls. Exposure of the surrounding environment to site contaminants also would be controlled by minimizing erosion and run-off, covering soil stockpiles, and implementing perimeter air monitoring.

5.3.2 Compliance with ARARs

No chemical-specific ARARs were identified for this alternative. The alternative is expected to comply with all identified location- and action-specific ARARs, including those governing erosion and sediment control, storm water management, fugitive dust emissions, and hazardous waste generation and management. If the soil is determined to contain RCRA hazardous waste, this alternative would need to meet RCRA land disposal restriction (LDR) alternative treatment standards for soil prior to off-site land disposal.

5.3.3 Long-Term Effectiveness and Permanence

This alternative would result in all soil with contaminant concentrations above cleanup levels to be excavated and disposed of in an off-site landfill. Lead contaminated soil would be stabilized by mixing the soil with a phosphate mineral ex situ. Excavated soils would be disposed, consistent with 40 CFR 300.440, in a TSDF that is acceptable to the USEPA. If the excavated soil is characterized as RCRA hazardous, the soil would be stabilized by the RCRA Subtitle C hazardous waste landfill and then deposited in the landfill. If the soil is not RCRA hazardous (i.e., stabilized soil), the soil would be disposed of directly into a sanitary landfill. Sanitary landfills are lined and capped such that the residential human health hazard presented by the soils would be controlled. Even after closure of the sanitary landfill, the soils would be controlled as part of landfill management.

Therefore, this alternative would not require future action to manage the risk of untreated waste or treatment residuals with regard to site soil. This alternative is considered to be permanent.

5.3.4 Reduction of Toxicity, Mobility, or Volume through Treatment

This alternative involves lead stabilization. To reduce the mobility of lead in affected soil, lead contaminated soil would be stabilized with a phosphate mineral. Stabilization would not reduce the toxicity or volume of lead in the soil. All soil with contaminant concentrations above cleanup levels would be excavated and disposed at either a local sanitary landfill or a permitted treatment, storage, disposal facility (TSDF). Based on the disposal requirements for the TSDF, off-site treatment to stabilize hazardous constituents may be performed at the RCRA landfill. Toxicity, mobility, and volume of site contaminants would not be significantly reduced by this alternative.

5.3.5 Short-Term Effectiveness

Worker exposure to contaminants during implementation of this alternative would be controlled by implementation of a site-specific HSP.

Adherence to the HSP would prevent contact with and inhalation of contaminants through the use of controls such as chemical-resistant clothing and respiratory protection. Exposure of the surrounding community and environment to site contaminants would also be controlled by minimizing run-off and dust emissions and implementing perimeter air monitoring. Physical risks to members of the community are minimal since the site is in a fenced, restricted area; however, truck traffic would increase. The time required to implement this alternative is estimated to be four months after mobilizing to the site.

5.3.6 Technical Feasibility

No significant technical or operational difficulties are anticipated in implementing this alternative. The alternative consists of well-established excavation and soil-handling processes. This alternative is expected to be an effective, reliable, and permanent option for addressing contaminated soil at 2BG.

5.3.7 Administrative Feasibility

It is anticipated that administrative difficulties would be encountered with this alternative due to the proposed shipping of large quantities of waste outside of Erie County.

5.3.8 Availability of Services and Materials

All personnel, equipment, and services required to implement this alternative are readily available in the vicinity of the site.

5.3.9 State Acceptance

It is not anticipated that the State of Ohio would have technical or administrative concerns with this alternative.

5.3.10 Community Acceptance

A potential concern that the community may have with this alternative is fugitive air emissions and a temporary increase in truck traffic in the vicinity of the site. Implementation of air monitoring and dust/contaminant suppression techniques would be important in gaining the community's acceptance of this alternative. A total of 210 truckloads of soil would be removed from the site with either a dump truck or a truck loaded with an intermodal container. Approximately 20 trips by trucks would be made into and out of the site on a daily basis for approximately one month. The dump trucks would be passing through southern Sandusky and the town of Milan. The intermodal trucks would travel approximately 10 miles on local and state roads (US-250, OH-2, and

OH-4) in route to Interstate 80. This additional truck traffic would potentially pose a safety hazard and noise/dust nuisance to the local residents.

5.3.11 Cost

The total capital cost for Alternative 2 is estimated to be \$1,286,000. Table 5-1 presents a summary of the cost estimate for this alternative. Supporting information is found in Appendix C.

5.4 Alternative 3: ex-situ treatment

5.4.1 Overall Protection of Public Health and Environment

This alternative is expected to effectively reduce risks to human health and the environment by combining excavation and on-site treatment of contaminated soil at 2BG. Lime treatment of TNT, DNT, Benzo(a)pyrene, and PCB would result in significant reduction of soil contaminants, and phosphate stabilization of lead contamination would significantly reduce the mobility of the lead. Treated soil that does not contain stabilized lead would be used as on-site backfill material. Treated soil with stabilized lead would be disposed as non-hazardous waste at a local sanitary landfill. Worker exposure to contaminants during implementation of this alternative would be controlled by following a site-specific HSP. Adherence to the requirements of the HSP would prevent contact with and inhalation of contaminants through the use of controls such as personal protective equipment (PPE). Exposure of the surrounding environment to site contaminants also would be controlled by minimizing erosion and run-off, covering soil stockpiles, and containment of the lime-soil slurry in on-site tanks during treatment.

5.4.2 Compliance with ARARs

No chemical-specific ARARs were identified for this alternative. The alternative is expected to comply with all identified location- and action-specific ARARs, including those governing erosion and sediment control, storm water management, fugitive dust emissions, and hazardous waste generation and management.

If it is determined that the soil contains RCRA hazardous waste, then excavation of the soil from the area of contamination (AOC) and subsequent treatment in a on-site mixer or tank would be considered treatment in a RCRA tank and would trigger RCRA tank requirements as ARARs and the need to meet RCRA LDR alternative treatment standards for soil prior to subsequent on-site re-use or off-site disposal.

5.4.3 Long-Term Effectiveness and Permanence

This alternative would result in all soil with contaminant concentrations above soil risk-based thresholds being excavated, treated, and dispositioned. Treated soil with stabilized lead would be disposed off-site. Treated soil that meets the thresholds for residential land use would be used as backfill at 2BG. Therefore, no future action would be required for the site as the risk associated with contaminants would be removed. This alternative is considered to be permanent.

5.4.4 Reduction of Toxicity, Mobility, or Volume through Treatment

This alternative involves two ex-situ treatment processes: lead stabilization and hydrated lime treatment. To reduce the mobility of lead in affected soil, lead contaminated soil would be stabilized with a phosphate mineral. Stabilization would not reduce the toxicity or volume of lead in the soil. Lime treatment of contaminated soil is likely to reduce concentrations of TNT by approximately 90%, DNT by approximately 70%, and Benzo(a)pyrene by 40%, and PCB by approximately 80%. This treatment through alkaline hydrolysis would reduce the toxicity, mobility, and volume of hazardous contaminants by reducing the concentrations of each constituent within the soil. As the bulk of the treated soil is likely to be suitable for use as backfill at 2BG, this treatment process also reduces the volume of waste requiring off-site disposal. Approximately 278 CY of soil would not be treated on site. Instead this soil would be stabilized off-site at a TSDF. Therefore, this alternative satisfies the USEPA's preference for treatment.

5.4.5 Short-Term Effectiveness

Worker exposure to contaminants during implementation of this alternative would be controlled by following a site-specific HSP. This plan would prevent contact with and inhalation of contaminants through the use of controls. Exposure of the surrounding community and environment to site contaminants would also be controlled by minimizing run-off and dust emissions, covering soil stockpiles, and containment of the lime-soil slurry in on-site tanks during treatment. Physical risks to members of the community are minimal since the site is in a fenced, restricted area. The time required to implement this alternative is estimated to be five months after mobilizing to the site.

5.4.6 Technical Feasibility

No significant technical or operational difficulties are anticipated in implementing this alternative. Alkaline hydrolysis is a well established method for the destruction of explosive compounds. However, to effectively reduce the current levels of DNT in the soil during treatment, longer residence times may be necessary for some soil treatment batches.

In order to manage this uncertainty, field screening would be required to evaluate real-time reduction of nitroaromatic concentrations. An evaluation of the potential for treatment to achieve the waste acceptance criteria for the local sanitary landfill was conduced. Based on this evaluation, approximately 278 CY of contaminated soil at 2BG would be characterized as hazardous even after the treatment technologies selected for this alternative are applied. Therefore, this contaminated soil would be excavated and disposed of at a permitted TSDF, and no on-site treatment would be utilized for this soil.

An approximately 3-acre staging and treatment area would need to be established for the treatment equipment and tanks/roll off boxes. Implementation of this alternative during the summer months is preferred, since this would facilitate drying of lime treated soil and excessive rainfall would be less likely.

This alternative is expected to be an effective, reliable, and permanent option for addressing contaminated soil at 2BG.

5.4.7 Administrative Feasibility

It is anticipated that minor administrative difficulties would be encountered with this alternative due to the proposed shipping of a small amount of waste outside of Erie County. This alternative would not require easements, right-of-way agreements, real estate acquisition, zoning variances, or a statutory limit exemption. Neutralized process/treatment water would have to be approved for discharge to the creek north of the site or a local publicly owned treatment works (POTW) in accordance with State regulations. It is anticipated that administrative difficulties would be encountered with this alternative due to the proposed shipping of large quantities of waste outside of Erie County.

5.4.8 Availability of Services and Materials

All personnel, equipment, and services required to implement this alternative are readily available in the vicinity of the site.

5.4.9 State Acceptance

It is not anticipated that the State of Ohio would have technical or administrative concerns with this alternative.

5.4.10 Community Acceptance

It is not anticipated that the local community would have concerns with this alternative.

5.4.11 Cost

The total capital cost for Alternative 3 is estimated to be \$1,509,000. Table 5-2 presents a summary of the cost estimate for this alternative. Supporting information is provided in Appendix C.

5.5 Alternative 4: in situ treatment

5.5.1 Overall Protection of Public Health and Environment

This alternative is expected to effectively reduce risks to human health and the environment by in-situ treating contaminated soil at 2BG and disposing of soil stabilized with lime off site. Contaminants would be significantly reduced through treatment by this alternative. Field screening and confirmation sampling would be used to verify that the treated soil left in place meets the thresholds for residential land use. Worker exposure to contaminants during implementation of this alternative would be controlled by following a site-specific HSP. Adherence to the requirements of the HSP would prevent contact with and inhalation of contaminants through the use of controls. Exposure of the surrounding environment to site contaminants also would be controlled by minimizing erosion and run-off.

5.5.2 Compliance with ARARs

No chemical-specific ARARs were identified for this alternative. The alternative is expected to comply with all identified location- and action-specific ARARs, including those governing erosion and sediment control, storm water management, fugitive dust emissions, and hazardous waste generation and management.

In situ treatment of the soil with lime to reduce TNT, DNT, benzo(a)pyrene, and PCB levels would not trigger RCRA LDR alternative treatment standards for soil since the soil is not removed from the AOC. Ex situ treatment of certain soils for lead stabilization, however, would trigger RCRA LDRs if the soil is determined to contain RCRA characteristic waste at the point of generation (i.e., when it is excavated); such soils would need to meet these treatment standards prior to off-site disposal.

5.5.3 Long-Term Effectiveness and Permanence

This alternative would result in all soil with contaminant concentrations above soil risk-based thresholds being treated and off-site disposal of any soil that does not meet the thresholds for residential use after treatment. As the long-term stability (i.e., the potential that the material would degrade under site conditions) of the stabilized lead contaminated soil is uncertain, this soil would also be disposed off-site as non-hazardous

waste. Therefore, no future action would be required for the site as the risk associated with contaminants would be removed. This alternative is considered to be permanent.

5.5.4 Reduction of Toxicity, Mobility, or Volume through Treatment

This alternative includes the same two treatment processes described for Alternative 3 except that the treatment processes are implemented at the site. As described for Alternative 3, this alternative satisfies the USEPA's preference for treatment by reducing the toxicity, mobility, and volume of hazardous contaminants in the soil. Approximately 278 CY of soil would not be treated on site. Instead this soil would be stabilized off-site at a TSDF.

5.5.5 Short-Term Effectiveness

Worker exposure to contaminants during implementation of this alternative would be controlled by implementation of a site-specific HSP. Adherence to the HSP would prevent contact with and inhalation of contaminants through the use of controls such as dust suppression. Exposure of the surrounding community and environment to site contaminants would also be controlled by minimizing run-off and dust emissions. Physical risks to members of the community are minimal since the site is in a fenced, restricted area. The time required to implement this alternative is estimated to be four months.

5.5.6 Technical Feasibility

No significant technical or operational difficulties are anticipated in implementing this alternative. Alkaline hydrolysis is a well established method for the destruction of explosive compounds. To effectively reduce the current levels of DNT in the soil, several applications of the hydrated lime may be required for each area, and several passes with the rotovator/tiller would also be likely to ensure that thorough mixing is achieved. In order to manage this uncertainty, field screening would be required to evaluate real-time reduction of nitroaromatic concentrations. Implementation of this alternative during the summer months is preferred, since excessive rainfall would be less likely. This alternative is expected to be an effective, reliable, and permanent option for addressing contaminated soil at 2BG.

An evaluation of the potential for treatment to achieve the waste acceptance criteria for the local sanitary landfill was conduced. Based on this evaluation, approximately 278 CY of contaminated soil at 2BG would be characterized as hazardous even after the treatment technologies selected for this alternative are applied. Therefore, this contaminated soil

would be excavated and disposed at a permitted TSDF, and no on-site treatment would be utilized for this soil.

5.5.7 Administrative Feasibility

It is anticipated that minor administrative difficulties would be encountered with this alternative due to the proposed shipping of a small amount of waste outside of Erie County. This alternative would not require easements, right-of-way agreements, real estate acquisition, zoning variances, or a statutory limit exemption.

5.5.8 Availability of Services and Materials

All personnel, equipment, and services required to implement this alternative are readily available in the vicinity of the site.

5.5.9 State Acceptance

It is not anticipated that the State of Ohio would have technical or administrative concerns with this alternative.

5.5.10 Community Acceptance

It is not anticipated that the local community would have concerns with this alternative.

5.5.11 Cost

The total capital cost for Alternative 4 is estimated to be \$1,106,000. Table 5-3 presents a summary of the cost estimate for this alternative. Supporting information is provided in Appendix C.

5.6 Alternative 5: Composting

5.6.1 Overall Protection of Public Health and Environment

This alternative is expected to effectively reduce risks to human health and the environment by combining excavation and on-site biological treatment of contaminated soil at 2BG. Nitroaromatic contaminants would be significantly reduced through treatment by this alternative. Worker exposure to contaminants during implementation of this alternative would be controlled by following a site-specific HSP. Adherence to the requirements of the HSP would prevent contact with and inhalation of contaminants through the use of controls. Exposure of the surrounding environment to site contaminants also would be controlled by minimizing erosion and run-off and air monitoring.

5.6.2 Compliance with ARARs

No chemical-specific ARARs were identified for this alternative. The alternative is expected to comply with all identified location- and action-specific ARARs, including those governing erosion and sediment control, storm water management, fugitive dust emissions, air monitoring, and hazardous waste generation and management.

In situ treatment of the soil with lime to reduce TNT, DNT, benzo(a)pyrene, and PCB levels and windrow composting to reduce DNT levels would not trigger RCRA LDR alternative treatment standards for soil since the soil is not removed from the AOC. Water collected in a frac tank from the drainage area is considered removed from the AOC and would be tested to ensure it does not contain RCRA characteristic waste prior to re-using it to spray the compost pile.

Ex situ treatment of certain soils for lead stabilization would trigger RCRA LDRs if the soil is determined to contain RCRA characteristic waste at the point of generation (i.e., when it is excavated); such soils would need to meet these treatment standards prior to off-site disposal.

5.6.3 Long-Term Effectiveness and Permanence
This alternative would result in all soil with contaminant concentrations above soil risk-based thresholds being excavated, stabilized and composted as required, and dispostioned. As the long-term stability (i.e., the potential that the material would degrade under site conditions) of the stabilized lead contaminated soil is uncertain, this soil would also be disposed of off-site. Therefore, no future action would be required for the site as the risk associated with contaminants would be removed. This alternative is considered to be permanent.

5.6.4 Reduction of Toxicity, Mobility, or Volume through Treatment

This alternative involves three treatment processes: windrow composting, lead stabilization, and in situ hydrated lime treatment. The 2BG soil with higher concentrations of DNT (approximately 278 CY) would be composted to reduce concentrations of DNT. This treatment through microbial destruction would reduce the toxicity and mobility of nitroaromatic constituents in the soil being treated. As composting significantly increases the volume of waste material through the addition of bulking agents and organic material, this treatment process increases the volume of waste requiring off-site disposal. As described for Alternative 3, stabilization would reduce the mobility of lead in affected soil and lime treatment would reduce the contaminant concentrations of nitroaromatics, Benzo(a)pyrene, and PCBs. Therefore, this alternative satisfies the USEPA's preference for treatment.

5.6.5 Short-Term Effectiveness

Worker exposure to contaminants and potential off-gas during implementation of this alternative would be controlled by implementation of a site-specific HSP. Adherence to the HSP would prevent contact with and inhalation of contaminants through the use of controls such as dust suppression and air monitoring. Exposure of the surrounding community and environment to site contaminants would also be controlled by minimizing run-off, dust emissions, and air monitoring. Physical risks to members of the community are minimal since the site is in a fenced, restricted area. The time required to implement this alternative is estimated to be six months after mobilizing to the site.

5.6.6 Technical Feasibility

No significant technical or operational difficulties are anticipated in implementing this alternative. Windrow composting is a well established method for the destruction of nitroaromatics. To effectively reduce the current levels of DNT in the soil, a bench-scale study would be required to identify the most effective parameters for composting. In addition, routine monitoring of the composting material would be necessary to evaluate the progress of the treatment. Implementation of this alternative during the summer months is preferred, since excessive rainfall would be less likely. This alternative is expected to be an effective, reliable, and permanent option for addressing contaminated soil at 2BG.

5.6.7 Administrative Feasibility

It is not anticipated that administrative difficulties would be encountered with this alternative. The alternative would not require off-site RCRA waste permits, easements, right-of-way agreements, real estate acquisition, zoning variances, or a statutory limit exemption.

5.6.8 Availability of Services and Materials

All personnel, equipment, and services required to implement this alternative are readily available in the vicinity of the site.

5.6.9 State Acceptance

It is not anticipated that the State of Ohio would have technical or administrative concerns with this alternative.

5.6.10 Community Acceptance

It is not anticipated that the local community would have concerns with this alternative.

5.6.11 Cost

The total capital cost for Alternative 4 is estimated to be \$1,360,000. Table 5-4 presents a summary of the cost estimate for this alternative. Supporting information is found in Appendix C.

6.0 comparative analysis of removal action alternatives

This section contains a comparative analysis of alternatives that evaluates the relative performance of each alternative in relation to each of the criteria addressed in Section 5.0. The purpose of the comparative analysis is to identify the advantages and disadvantages of each alternative relative to one another so that key tradeoffs that would affect the alternative selection can be identified. These criteria comparisons are summarized in Table 6-1 and are addressed in further detail below.

6.1 Overall Protection of Public Health and Environment

All of the alternatives, with the exception of Alternative 1, would permanently treat or remove contaminated soil, thereby reducing cancer and toxicity risks to human receptors to within the respective OEPA risk management ranges. Alternative 1 does not employ removal, containment, or treatment response actions that would mitigate the impact of source areas on receptors.

6.2 Compliance With ARARs

All of the action alternatives would comply with location and actionspecific ARARs, including those governing erosion and sediment control, storm water management, fugitive dust emissions, air monitoring, and hazardous waste generation and management. No chemical specific ARARs were identified.

6.3 Long-Term Effectiveness and Permanence

All alternatives, with the exception of Alternative 1, would reduce the residual risk at the site such that unrestricted or residential land use would be allowed. No long-term controls would be required for Alternatives 2 through 5 as these alternatives are considered permanent.

6.4 Reduction of Toxicity, Mobility, or Volume Through Treatment

Alternatives 3, 4, and 5 include treatment measures that would satisfy the statutory preference for selecting remedial actions that employ treatment technologies that permanently and significantly reduce the toxicity, mobility, or volume of hazardous substances as their principal element. Although Alternative 2 would remove contamination from the site and includes some stabilization efforts on-site and at the TSDF, this alternative

does not result in any reduction of contaminant mass. Stabilization would minimize the potential for contaminants to leach into the environment. Alternative 1 does not employ treatment and would have no effect on the toxicity, volume, or mobility of soil contamination.

6.5 Short-Term Effectiveness

Implementing a site-specific HSP and minimizing off-site migration of contaminants would minimize potential risks to workers and the surrounding community. There would be some risks, however, due to the heavy equipment operating on site and the presence of contaminants. Alternatives 2, 3, and 4 include the greatest amount of truck traffic (i.e., hauling waste, in-bound supplies and equipment, etc.). Short term effectiveness is not relevant to Alternative 1 because no action would be taken.

No threatened or endangered animal or plant species would be significantly affected or destroyed by Alternatives 2 through 5. There would be short-term disturbances to ecological habitats as a result of the proposed remediation (i.e., tree and brush clearing, excavation, etc.); however, once the action is completed the site would be restored with a vegetative cover and it is anticipated that over time displaced species would recolonize the area.

Alternatives 5 would require approximately six months for execution, while Alternatives 2, 3, and 4 would only require approximately four to five months.

6.6 TECHNICAL FEASIBILITY

Alternatives 3, 4 and 5 may require specific soil handling procedures, such as wetting, drying, and amending. Moreover, to effectively reduce the current levels of DNT in the soil during treatment for these alternatives, additional soil mixing, amendments, or longer residence times may be necessary. In order to manage this uncertainty, field screening would be required to evaluate real-time reduction of nitroaromatic concentrations. However, for Alternatives 3 and 4 it is anticipated that lime treatment would not effectively reduce contaminant concentrations in approximately 278 CY of soil to non-hazardous level. A bench-scale study would be required during the design phase of Alternative 5 to determine the most effective recipe for rapid destruction of nitroaromatic constituents in 2BG soil.

No significant technical or operational difficulties are anticipated in implementing either Alternatives 1 or 2.

6.7 Administrative Feasibility

Administrative difficulties are anticipated for Alternatives 2 through 4 as a result of the proposed shipping of hazardous waste outside of Erie County. Obtaining approval to use a facility other than the local sanitary landfill may cause delays in project schedule.

6.8 Availability of Services and Materials

All personnel, equipment, and services required to implement any of the alternatives are readily available for delivery to the site. Only standard construction or farming equipment is required for Alternatives 2 through 5. Treatment additives such as hydrated lime or phosphate mineral are available through several national vendors. Composting amendments are readily available from local vendors/farms.

6.9 State Acceptance

The State of Ohio is not expected to have any technical or administrative concerns regarding Alternatives 2 through 5. However, it is anticipated that Alternative 1 would not be acceptable to the state regulators.

6.10 Community Acceptance

A potential concern that the community may have with Alternative 2 is the increased truck traffic into and out of the site associated with excavation and disposal. The community is also unlikely to accept Alternative 1 as it does not address the soil contamination and is not protective of human health. It is unlikely that there would be any community concerns over the implementation of Alternatives 3, 4, and 5.

6.11 Cost

No cost would be incurred for Alternative 1 as no action would be performed.

The cost estimates for Alternatives 2 through 5 were prepared in a similar manner. The costs are based on upon estimates provided by regional companies (including local sanitary waste landfills and regionally available TSDFs) and cost factors from R.S. Means cost data publications applied to quantities in Appendix B. The cost for sampling and analysis of waste soil and confirmatory samples for the site are estimated based on previous projects completed with similar scope. Indirect costs (professional services) are based on the projected level of effort required to perform a detailed design and field oversight for each alternative.

The total cost for Alternative 2 is estimated at \$1,286,000. This estimate includes all major parts of the proposed remediation (site preparation, staging area set up, mobilization, excavation, stabilization, waste packaging, waste transportation and disposal, site restoration, and demobilization).

The total cost for Alternative 3 is estimated at \$1,509,000. This estimate includes all major parts of the proposed remediation (site preparation, staging area set up, mobilization, excavation, lime treatment, lead stabilization, waste packaging, waste transportation and disposal, site restoration, and demobilization).

The total cost for Alternative 4 is estimated at \$1,106,000. This estimate includes all major parts of the proposed remediation (site preparation, staging area set up, mobilization, lime treatment, lead stabilization, waste packaging, waste transportation and disposal, site restoration, and demobilization).

The total cost for Alternative 5 is estimated at \$1,360,000. This estimate includes all major parts of the proposed remediation (site preparation, staging area set up, mobilization, excavation, lime treatment, lead stabilization, windrow composting, waste packaging, waste transportation and disposal, site restoration, and demobilization).

The uncertainties and assumptions associated with the costs are as follows:

Final disposition of the 2BG property is unknown. An assumption has been made that a vegetative cover (e.g., grass) would be placed on the surface to allow the greatest flexibility for future use with minimal site maintenance costs.

Water required for treatment operations in Alternatives 3 through 5 is assumed to be pumped from the basin north of the 2BG site. If the basin is not available for use by the project, additional costs may be incurred if water must be trucked in from an off-site source. Process water collected from Alternatives 3 and 5 would be treated for neutralization as required, characterized, and discharged to the creek north of the site.

Costs associated with disposal of trees and brush removed during site clearing are not included. It is assumed that this organic material may be incorporated into the backfill, incorporated into the compost pile, or burned on-site.

During site restoration, the site would not be regraded to original grade, but rather an acceptable sloping grade to eliminate the requirement for purchasing backfill for Alternatives 2 through 5.

7.0 recommended removal action alternative

Alternative 4 is the preferred alternative for remediating contaminated soil at the 2BG site. This alternative was selected based on price, ease of implementation, and proven effectiveness of using lime to reduce all of the site contaminants with the exception of lead.

Alternative 1 was eliminated because it does not meet the remedial action objectives. Alternative 2 was eliminated due to a greater volume of waste requiring disposal at a RCRA facility outside of Erie County and higher cost. Alternative 3 was eliminated because of cost. Alternative 5 was eliminated because of cost and uncertainty regarding treatment effectiveness due to high concentrations of 2,4 DNT and the coarse nature of the burn layer material.

There are differences between the alternatives for cost and reduction of toxicity, mobility, or volume through treatment.

7.1 COST

The least expensive alternative is Alternative 4 because the associated activities require very little engineering design to implement, can be performed with only a few types of equipment, and can be accomplished with a small field crew in a relatively short amount of time. There is minimal cost impact if additional applications of lime were required should the reduction of contaminants not be as high as anticipated. The amount of lime could be doubled for the lifetime of the project for under \$3,000 and likewise, the treatment could be prolonged for an additional month for under \$50,000. The relatively low cost of this option helps to offset some of the uncertainties with the effectiveness of tilling. The relative risk involved with this option is minimal because of the limited up front expenditures.

The difference between the most expensive alternative and the least expensive action alternative is approximately \$400,000. This difference is not considered to be great, however, the accuracy typically achieved in such "study estimates" is +50 percent to -30 percent (USEPA 1988). It is believed a higher level of accuracy was achieved in the cost estimate performed for this EE/CA Report.

7.2 reduction of toxicity, mobility, or volume through treatment

Lime treatment is a proven method to reduce toxicity as demonstrated in the treatability study. Alternative 4 assumes 1 month of treatment to effectively reduce contaminants below the remedial objectives, which is fairly conservative considering the batch treatment effectively reduces site

contaminants within 24 hours. Alternative 4 offers a reasonable amount of flexibility to alter the treatment application as needed to ensure success.

7.3 Selection of the Preferred Alternative

Alternative 4 offers the lowest cost because of the minimal amount of engineering required. Lime treatment is a proven method for reducing concentrations of PCBs, PAHs, DNT, and TNT as demonstrated through batch experiments in a laboratory setting using 2BG soil. To offset the uncertainties associated with tilling, multiple applications of lime would be used to maximize contact with the soil. Frequent testing of the soil pH would be conducted to confirm adequate alkaline hydrolysis reactions are occurring and to make adjustments as needed.

Although some hazardous waste disposal is required in this alternative, the relative volume of hazardous waste is small. Further reduction of the toxicity of this hazardous waste would be performed by the TSDF using existing proven treatment methods that are more cost effective for small quantities of waste.

7.4 determination of removal schedule

The following components and the associated durations for Alternative 4 are as follows:

Preparation of Planning Documents and Engineering 4 months Implementation of Field Activities 4 months Preparation of Post-Action Report 4 months

REFERENCES

Jacobs Engineering Group, 2006 *Final Site Characterization Report*, Remedial Investigation, Part 1, at Reservoir No. 2 Burning Ground, Former Plum Brook Ordnance Works, Sandusky, Ohio.

U.S. Environmental Protection Agency, 1993. *Guidance on Conducting Non-Time-Critical Removal Actions Under CERCLA*, <u>EPA/540-R-93-057</u>, Office of Emergency and Remedial Response, Washington, DC.

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (<i>DD-MM-YYYY</i>) September 2007	2. REPORT TYPE Final report	3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE		5a. CONTRACT NUMBER	
Evaluation of Lime and Persulfa Plum Brook Ordnance Works (S	5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
Victor F. Medina, Scott A. Wais and Michael Jones	5e. TASK NUMBER		
and whender jones		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME	(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER	
	Engineer Research and Development Center, 3909	EDDG/EL ED 05 10	
Halls Ferry Road, Vicksburg, MS 3918 Division, 119 Monument Place, Vicks State, MS 39096-7500	ERDC/EL TR-07-19		
,			
9. SPONSORING / MONITORING AGENC	10. SPONSOR/MONITOR'S ACRONYM(S)		
U.S. Army Corps of Engineers			
Washington, DC 20314-1000		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
42 DISTRIBUTION / AVAIL ADJUSTS STAT			

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The former Plum Brook Ordnance Works in Sandusky, OH, manufactured explosives from 1941 to 1945. The Reservoir No. 2 Burning Ground has soil contaminated with explosives, 2,4,6-trinitrotoluene (TNT) and 2,4-/2,6-dinitrotoluene (DNT), a polychlorinated biphenyl (PCB), Araclor 1260, polycyclic aromatic hydrocarbons (PAHs), particularly benzo(a)pyrene, and lead. The U.S. Army Engineer Research and Development Center (ERDC) Environmental Laboratory (EL) investigated a series of chemical based treatments to address this complex matrix. Lime treatment was tested to treat the explosives. Advanced oxidation (persulfate treatment and Fenton's reagent) was studied for treatment of PCBs and PAHs. Phosphate treatment was investigated for stabilizing lead. Lime treatment degraded 98 percent of TNT, 75 percent of DNT, and 80 percent of PCBs. There was minimal removal of PAHs (41 percent). Similar removal levels were found for persulfate treatment and lime followed by persulfate. Lower destruction rates of explosives were obtained by a single Fenton's reagent treatment, probably due to rapidity of the reaction. Loss percentages were roughly the same for highly contaminated soils (burn layer) and less contaminated soil (west surface soil). Treatments of the most contaminated soil (burn layer soils) did not meet Preliminary Remediation Goals for explosives or PCBs. Phosphate treatment was effective at stabilizing the lead in the soil, reducing lead toxicity characteristic leaching procedure concentrations below 5 mg/L.

15. SUBJECT TERMS Persulfate			2,4,6-TNT		
Plum Brook Ordnance Works PCB			2,4/2,6-DNT		
Lime PAH					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED		116	area code)